

# ATOMIC STRUCTURE BONDING AND HYDROCARBONS

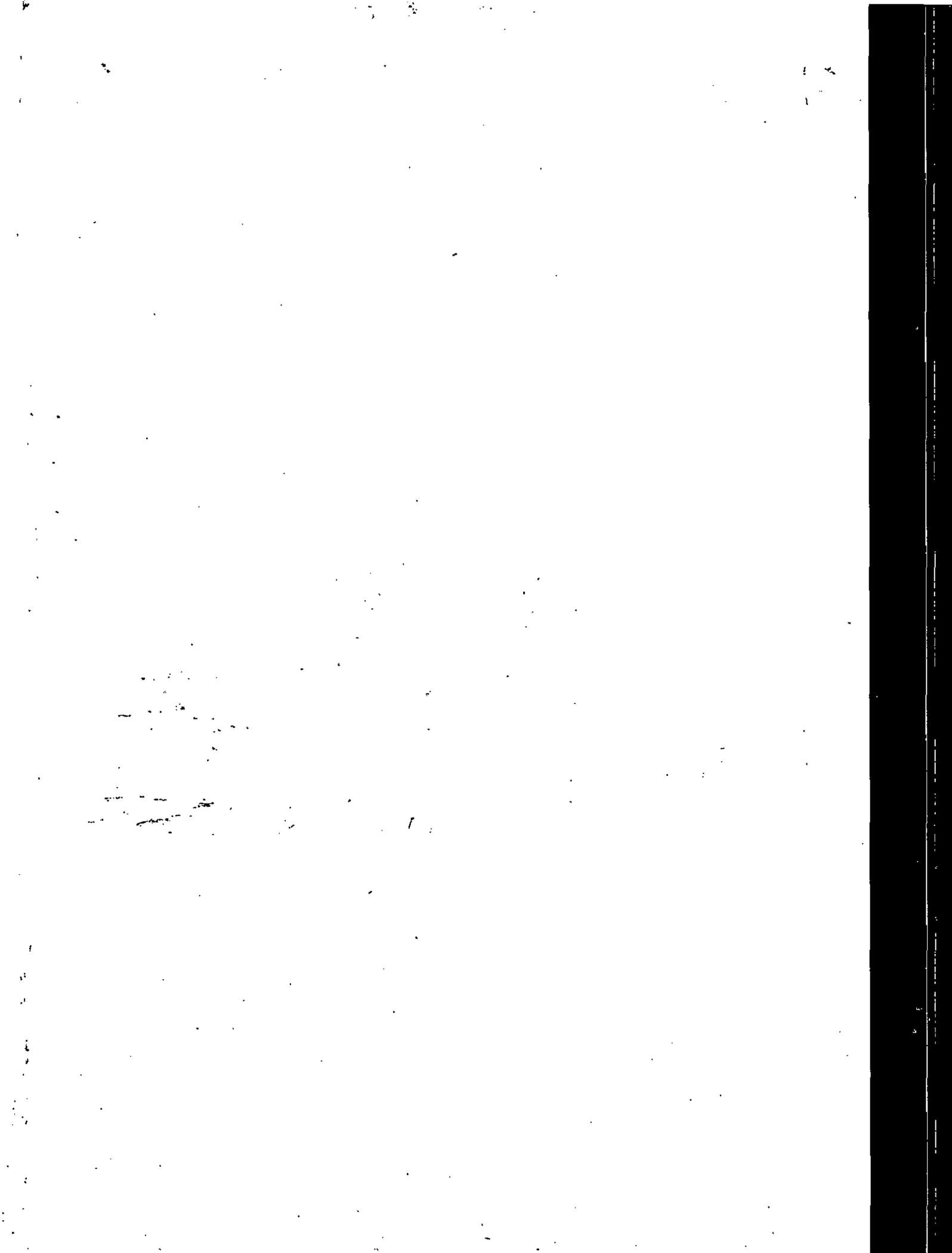


**DIRECTORATE OF DISTANCE EDUCATION**

**SWAMI VIVEKANAND**

**SUBHARTI UNIVERSITY**

**Meerut (National Capital Region Delhi)**



# **ATOMIC STRUCTURE, BONDING AND HYDROCARBONS**

**B.Sc. PCM-103**

*Self Learning Material*



**Directorate of Distance Education**

**SWAMI VIVEKANAND SUBHARTI UNIVERSITY  
MEERUT-250 005  
UTTAR PRADESH**

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**EDITION : 2021**

# PREFACE

In this course, we shall deal with various aspects of Atomic Structure Bonding and Hydrocarbons

The book consists of the following units :

- Atomic Structure
- Chemical Bonding
- Fundamentals of Organic Chemistry and Stereochemistry
- Chemistry of Aliphatic Hydrocarbons

## SYLLABUS ATOMIC STRUCTURE, BONDING AND HYDROCARBONS

### UNIT-1 : Atomic Structure

Bohr's theory, its limitations and atomic spectrum of hydrogen atom. Wave mechanics: de Broglie equation, Heisenberg's Uncertainty Principle and its significance, Schrödinger's wave equation, significance of  $\psi$  and  $\psi^2$ . Quantum numbers and their significance. Normalized and orthogonal wave functions. Sign of wave functions. Radial and angular wave functions for hydrogen atom. Radial and angular distribution curves. Shapes of s, p, d and f orbitals. Contour boundary and probability diagrams.

Pauli's Exclusion Principle, Hund's rule of maximum multiplicity, Aufbau's principle and its limitations, Variation of orbital energy with atomic number.

### UNIT 2 : Chemical Bonding

**1. Ionic bond:** General characteristics, types of ions, size effects, radius ratio rule and its limitations. Packing of ions in crystals. Born-Landé equation with derivation and importance of Kapustinskii expression for lattice energy. Madelung constant, Born-Haber cycle and its application, Solvation energy.

**2. Covalent bond:** Lewis structure, Valence Bond theory (Heitler-London approach). Energetics of hybridization, equivalent and non-equivalent hybrid orbitals. Bent's rule, Resonance and resonance energy, Molecular orbital theory. Molecular orbital diagrams of diatomic and simple polyatomic molecules  $N_2$ ,  $O_2$ ,  $C_2$ ,  $B_2$ ,  $F_2$ , CO, NO, and their ions; HCl,  $BeF_2$ ,  $CO_2$ , (idea of s-p mixing and orbital interaction to be given). Formal charge, Valence shell electron pair repulsion theory (VSEPR), shapes of simple molecules and ions containing lone pairs and bond pairs of electrons, multiple bonding ( $\sigma$  and  $\pi$  bond approach) and bond lengths. Covalent character in ionic compounds, polarizing power and polarizability. Fajan's rules and consequences of polarization. Ionic character in covalent compounds

Bond moment and dipole moment. Percentage ionic character from dipole moment and electronegativity difference.

### UNIT 3 : Fundamentals of Organic Chemistry

Physical Effects, Electronic Displacements: Inductive Effect, Electromeric Effect, Resonance and Hyperconjugation. Cleavage of Bonds: Homolysis and Heterolysis.

Structure, shape and reactivity of organic molecules: Nucleophiles and electrophiles. Reactive Intermediates: Carbocations, Carbanions and free radicals.

Strength of organic acids and bases: Comparative study with emphasis on factors affecting  $pK$  values. Aromaticity: Benzenoids and Hückel's rule.

### Stereochemistry

Conformations with respect to ethane, butane and cyclohexane. Interconversion of Wedge Formula, Newman, Sawhorse and Fischer projections. Concept of chirality, (upto two carbon atoms). Configuration: Geometrical and Optical isomerism; Enantiomerism, Diastereomerism and Meso compounds). Threo and erythro; D and L; cis - trans nomenclature; CIP Rules: R/S (for upto 2 chiral carbon atoms) and E/Z nomenclature (for upto two C=C systems). (10 Hours)

### UNIT 4 : Chemistry of Aliphatic Hydrocarbons

**Carbon-Carbon sigma bonds :** Chemistry of alkanes: Formation of alkanes, Wurtz Reaction, Wurtz-Fittig Reactions, Free radical substitutions: Halogenation -relative reactivity and selectivity.

**Carbon-Carbon pi bonds:** Formation of alkenes and alkynes by elimination reactions, Mechanism of  $E_1$  and  $E_2$  reactions. Saytzeff and Hofmann eliminations.

**Reactions of alkenes:** Electrophilic additions their mechanisms (Markownikoff/ Anti Markownikoff addition), mechanism of oxymercuration-demercuration, hydroborationoxidation, ozonolysis, reduction (catalytic and Chemical), syn and anti-hydroxylation (oxidation). 1,2- and 1,4-addition reactions in conjugated dienes and, Diels-Alder reaction; Allylic and benzylic bromination and mechanism, e.g. propene, 1-butene, toluene, ethyl benzene.

**Reactions of alkynes:** Acidity, Electrophilic and Nucleophilic additions. Hydration to form carbonyl compounds, Alkylation of terminal alkynes.

### Course Outcome(s)

- C01 Understanding the atomic structure, basics of quantum chemistry and its applications.
- C02 Explaining theories of chemical bonding and molecular structure.
- C03 Gathering basic knowledge of organic chemistry.
- C04 Learning the basic principles of stereochemistry.
- C05 Illustrate the preparative methods of saturated and unsaturated hydrocarbons.

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# UNIT

# 1

## ATOMIC STRUCTURE

### STRUCTURE

- Bohr's Theory and Limitations
- Atomic Spectrum of Hydrogen Atom
- Dual Nature of Matter
- Wave Mechanical Model
- Heisenberg's Uncertainty Principle
- Schrodinger Wave Equation
- Quantum Numbers
- Normalized and Orthogonal Wave Functions
- Radial and Angular Wave Function for Hydrogen Atom
- Radial and Angular Distribution Curves
- Shapes of s, p, d and f Orbitals
- Pauli's Exclusion Principle
- Hund's Rule of Maximum Multiplicity
- Aufbau Principle
  - Summary
  - Student Activity
  - Test Yourself
  - Answers

### LEARNING OBJECTIVES

After going this unit you will learn :

- The modern theory of the structure of the atom
- Atomic orbitals of different types
- Quantum numbers
- Radial and angular wave functions
- The principles for filling up of the electrons in different orbitals.

#### • 1.1. BOHR'S THEORY

In 1807 John Dalton proposed his famous atomic theory, according to Dalton, Matter is composed by very small particles called **atoms** and they are **indivisible**. However, the study of conductance of electricity through gases, development of radioactivity etc. provided a number of evidences which exhibit that atom is not indivisible, but consists of smaller fundamental particles, such as *electron* (charge :  $1.60206 \times 10^{-19}$  C, mass :  $9.1091 \times 10^{-31}$  kg), *proton* (charge :  $1.60206 \times 10^{-19}$  C, mass :  $1.6725 \times 10^{-27}$  kg) (about 1837 times of the electron), *neutron* (charge : nil, mass :  $1.6750 \times 10^{-27}$  kg). Different scientists proposed structure of atoms but not accepted.

In 1913 **Bohr** developed a theory based on quantum theory of radiation and law of classical mechanics to explain atomic spectra and structure of atom. His theory was based on the following postulates :

**Bohr's Postulates :**

(i) An atom has a number of stable orbits or stationary states, in which an electron can reside without the emission of radiant energy. Each orbit corresponds to certain energy level.

(ii) An electron may jump spontaneously from one orbit (energy level  $E_1$ ) to the other orbit (energy level  $E_2$ ) ( $E_2 > E_1$ ); then the energy change ( $\Delta E$ ) in the electron jump is given by Planck's equation :

$$\Delta E = E_2 - E_1 = h\nu \quad \dots (1)$$

or 
$$\frac{\Delta E}{h} = \nu = \frac{c}{\lambda} = c\bar{\nu} \quad \dots (2)$$

where  $h$  = Planck's constant,  $\nu$  = frequency of the light emitted,  $c$  = velocity of light,  $\lambda$  = wavelength of light and  $\bar{\nu}$  = wave number.

(iii) The motion of an electron in a circular orbit is restricted in such a manner that its angular momentum is an integral multiple of  $\frac{h}{2\pi}$ .

Thus, 
$$mvr = \frac{nh}{2\pi} \quad \dots (3)$$

where  $m$  = mass of the electron,  $v$  = velocity of the electron,  $r$  = radius of the orbit and  $n$  = an integer called **principal quantum number** of the electron.

(iv) A space around nucleus which contained orbits of equal energy and radius was called shell. These shells were numbered from inside to outwards as 1, 2, 3, 4 etc and called *K, L, M, N* etc. respectively.

On the basis of Bohr's theory of hydrogen atom, the radius,  $r$ , of the  $n$ th orbit ( $r_n$ ), the energy,  $E$ , of the  $n$ th orbit ( $E_n$ ) and velocity,  $V$  in the  $n$ th orbit ( $V_n$ ) of the electron are given by :

$$r_n = \frac{n^2 h^2}{4\pi^2 Z e^2 m} \quad \dots (4)$$

$$E_n = \frac{-2\pi^2 Z^2 m e^4}{n^2 h^2} = -\frac{Z e^2}{2r_n} \quad \dots (5)$$

and 
$$V_n = \frac{2\pi Z e^2}{nh} \quad \dots (6)$$

where  $m$  and  $e$  are the mass and charge of the electron,  $Z$  is the atomic number of the element and  $n$  is any integer as 1, 2, 3, ... which represents the number of main energy level. The above derivations have been carried out in c.g.s. system of units. In M.K.S. system of units (S.I. units), a constant  $K$  is used. In c.g.s. system  $K = 1$  but in SI system  $K = \frac{1}{4}\pi\epsilon_0 = 9 \times 10^9 \text{ N m}^2 \text{ c}^{-2}$ .  $\epsilon_0$  is called permittivity factor of the medium. For vacuum its value is  $8.854 \times 10^{-12} \text{ c}^2 \text{ N}^{-1} \text{ m}^{-2}$ .

Thus the equations 4, 5, 6 in SI units may be written as :

$$r_n = \frac{n^2 h^2}{4\pi^2 Z e^2 m K}$$

$$E_n = -\frac{2\pi^2 Z^2 m e^4 K^2}{n^2 h^2}$$

$$V_n = \frac{2\pi Z e^2 K}{nh}$$

Equation (5) is known as **Bohr equation** applicable to hydrogen and hydrogen like ions having only one electron viz.  $\text{He}^+$ ,  $\text{Li}^{2+}$ ,  $\text{Be}^{3+}$  etc.

If an electron drops from higher level  $n_2$  (with energy  $E_2$ ) to the lower level  $n_1$  (with energy  $E_1$ ) then the change in energy may be given as :

From eq. (5),

$$\begin{aligned}\Delta E &= E_2 - E_1 \\ &= \frac{2\pi^2 Z^2 me^4}{h^2} \left[ \frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \quad \dots (7)\end{aligned}$$

But from eq. 2,

$$\Delta E = h\nu = h\bar{\nu}c = \frac{2\pi^2 Z^2 me^4}{h^2} \left[ \frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

or

$$\bar{\nu} = \frac{2\pi^2 Z^2 me^4}{h^3 c} \left[ \frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \quad \dots (8)$$

or

$$\bar{\nu} = R_H Z^2 \left[ \frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \quad \dots (9)$$

where  $R_H$  is the **Rydberg's constant** and equal to  $2\pi^2 me^4 / h^3 c$ . Its value for hydrogen atom is  $1.09714 \times 10^7 \text{ m}^{-1}$ .

By substituting different values in the above equations we may derive that

**For hydrogen atom**

$$\begin{aligned}r_1 &= 0.529 \text{ \AA}, \\ r_n &= 0.529 \times n^2 \text{ \AA} \\ E_1 &= -2.179 \times 10^{-18} \text{ J/atom}, \\ E_n &= \frac{-2.179 \times 10^{-18}}{n^2} \text{ J/atom} \\ V_1 &= 2.1847 \times 10^6 \text{ m s}^{-1} \\ V_n &= \frac{2.1847 \times 10^6}{n} \text{ m s}^{-1}\end{aligned}$$

**For Hydrogen like ions**

$$\begin{aligned}r_1 &= \frac{0.529}{Z} \text{ \AA} \\ r_n &= 0.529 \times \frac{n^2}{Z} \text{ \AA} \\ E_1 &= -2.179 \times 10^{-18} Z^2 \text{ J/atom} \\ E_n &= -2.179 \times 10^{-18} \frac{Z^2}{n^2} \text{ J/atom} \\ V_1 &= 2.1847 \times 10^6 Z \text{ m s}^{-1} \\ V_n &= 2.1847 \times 10^6 \times \frac{Z}{n} \text{ m s}^{-1} \\ &\quad (Z = \text{atomic number of the atom})\end{aligned}$$

**Remember :**

1. The negative sign of  $E_n$  indicates that there is attraction between the electron and the nucleus of the atom. Thus work has to be done in order to remove an electron from its orbit.

2. Since  $E_n \propto \frac{1}{n^2}$  hence as the value of  $n$  increases less negative is the energy of the electron in it or the energy of the electron has more positive value.

3. Since in energy equation all the terms are constant except  $n$  hence for a definite value of  $n$ ,  $E_n$  is constant. It means the energy of an electron revolving in a particular orbit is definite.

## Some Parameters for Electron in a Hydrogen Atom

Orbit No.	Radius (Å)	Energy		Velocity $\text{ms}^{-1}$
		J/atom	eV/atom	
1.	0.529	$-2.179 \times 10^{-18}$	-13.56	$2.1847 \times 10^6$
2.	2.116	$-5.44 \times 10^{-18}$	-3.39	$1.0923 \times 10^6$
3.	4.761	$-0.242 \times 10^{-18}$	-1.51	$0.7282 \times 10^6$
4.	8.464	$-0.136 \times 10^{-18}$	-0.85	$0.5462 \times 10^6$
5.	13.225	$-0.087 \times 10^{-18}$	-0.544	$0.4369 \times 10^6$

**Merits of Bohr's Theory**

- Bohr's theory explains clearly the hydrogen spectrum.
- The experimental value of Rydberg constant for hydrogen ( $R_H$ ) is very close to the calculated value from Bohr's theory.
- The experimental value of the frequencies of the spectral lines of the hydrogen spectrum are in good agreement with the calculated value from Bohr's theory.
- The experimental values of radii and energies of different orbits in hydrogen atom are in good agreement with that of calculated values.

**Limitations of Bohr's Theory :**

- It cannot explain the spectra of atoms having more than one electron e.g., He, Li, Be etc.
- It failed to explain fine structure i.e. why there are number of component lines lying close together when the spectra of hydrogen is examined by a powerful spectroscope.
- Since there is uncertainty of the position and velocity of the electron hence the concept of electrons jumping from one orbit to another is not justified.
- This theory is based on two opposite theories such as quantum theory and law of classical mechanics.
- It is difficult to calculate the effects of the electrons upon the energy state of any one particular electron.
- It does not throw light on the distribution and arrangement of electrons in atoms as well as shape of the molecules, formed by the combination of atoms.

**Example 1.** Calculate the frequency, wave number and energy associated with photon of radiations having wavelength 5500 Å.

$$(h = 6.626 \times 10^{-34} \text{ J s and } c = 3 \times 10^8 \text{ m s}^{-1})$$

$$\text{Solution: Frequency, } \nu = \frac{c}{\lambda} = \frac{3 \times 10^8 \text{ m s}^{-1}}{5500 \times 10^{-10} \text{ m}}$$

$$= 5.45 \times 10^{14} \text{ s}^{-1}$$

$$\text{Wave number, } \bar{\nu} = \frac{\nu}{c} = \frac{5.45 \times 10^{14} \text{ s}^{-1}}{3 \times 10^8 \text{ m s}^{-1}}$$

$$= 1.8166 \times 10^6 \text{ m}^{-1}$$

$$\text{Energy of photon, } E = h\nu$$

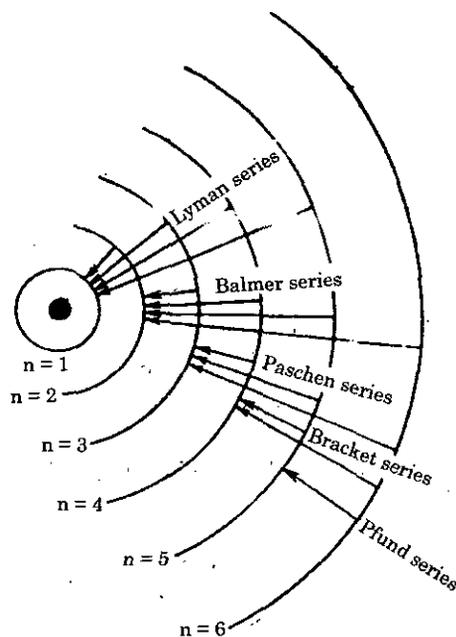
$$= (6.626 \times 10^{-34} \text{ J s}) (5.45 \times 10^{14} \text{ s}^{-1})$$

$$= 3.611 \times 10^{-19} \text{ J}$$

## • 1.2. HYDROGEN SPECTRUM

When hydrogen gas is taken in a discharged tube at low pressure and electric discharge is passed, red colour light is emitted. This light is analysed with the help of spectrograph; it is found to consist of a series of sharp lines in UV, Visible and IR regions. This series of lines is known as line or atomic spectrum of hydrogen.

Since no darkening between the lines is observed in hydrogen spectrum it means the hydrogen atom emits only specific and not all frequencies.



**Hydrogen spectrum**

In 1885, **Balmer** showed that if the lines of hydrogen spectrum of visible region are expressed in term of wave number ( $\bar{\nu}$  or  $\lambda^{-1}$ ) then the following formula may be used :

$$\bar{\nu}(\text{cm}^{-1}) = 109,677 \left( \frac{1}{2^2} - \frac{1}{n^2} \right)$$

where  $n = 3, 4, 5, \dots$

In 1890, **Rydberg** showed that the following formula may be used to give wave number of different lines observed in hydrogen spectrum :

$$\bar{\nu}(\text{cm}^{-1}) = 109,677 \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad \dots (10)$$

where  $n_1$  and  $n_2$  are integers such that  $n_1 < n_2$ . This is summarised in the table

**Hydrogen Spectrum**

Lyman series	$n_1 = 1, n_2 = 2, 3, 4$ etc.	in the UV region
Balmer series	$n_1 = 2, n_2 = 3, 4, 5$ etc.	in the Visible region
Paschen series	$n_1 = 3, n_2 = 4, 5, 6$ etc.	in the IR region
Brakett series	$n_1 = 4, n_2 = 5, 6, 7$ etc.	in the far IR region
Pfund series	$n_1 = 5, n_2 = 6, 7, 8$ etc.	in the far IR region.

**Example 2.** Find out the number of waves made by a Bohr electron in one complete revolution in its 3rd orbit.

**Solution.** By Bohr's law

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

$$n = \frac{mvr}{h/2\pi} = \frac{2\pi r}{h/mv}$$

Now by de Broglie's equation,

$$\lambda = \frac{h}{mv}$$

and

$$2\pi r = \text{circumference}$$

So

$$n = Z = \frac{\text{circumference}}{\lambda}$$

$$= \text{No. of waves}$$

Hence no. of waves in one complete revolution = 3.

**Example 3.** Calculate the wavelength of radiation emitted, producing a line in Lyman series, when an electron falls from fourth stationary state in hydrogen atom ( $R_H = 1.1 \times 10^7 \text{ m}^{-1}$ )

**Solution.**  $\therefore \bar{\nu} = R_H \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$

or  $\frac{1}{\lambda} = R_H \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$

or  $\frac{1}{\lambda} = 1.1 \times 10^7 \text{ m}^{-1} \left( \frac{1}{1^2} - \frac{1}{4^2} \right)$

$$= 1.1 \times 10^7 \text{ m}^{-1} \left( 1 - \frac{1}{16} \right)$$

$$= 1.1 \times \frac{15}{16} \times 10^7 \text{ m}^{-1}$$

or  $\lambda = \frac{16 \times 10^{-7}}{16.5} \text{ m}$

$$= 9.7 \times 10^{-8} \text{ m.}$$

**Example 4.** Calculate Bohr's radius (radius of first orbit for hydrogen), the energy and velocity of electron in first orbit of hydrogen atom.

**Solution :** Radius of an orbit is given by the expression (eq. 4)

$$r_n = \frac{n^2 h^2}{4\pi^2 Z m e^2}$$

$$r_1 = \frac{(1)^2 (6.626 \times 10^{-27} \text{ ergs})^2}{4(3.14)^2 (1)(9.109 \times 10^{-28} \text{ g})(4.803 \times 10^{-10} \text{ e.s.u.})^2}$$

$$= 0.529 \times 10^{-8} \text{ cm} = 0.529 \text{ \AA.}$$

We know that  $r_1$  i.e. radius of first orbit for hydrogen is also known as Bohr's radius and denoted by  $a_0$ . The value of  $r_n = a_0 \times n^2$ .

Energy of an orbit is given by the expression (eq. 5) :

$$E_n = -\frac{Ze^2}{2r_n}$$

or

$$E_1 = -\frac{Ze^2}{2r_1}$$

$$= -\frac{(1)(4.803 \times 10^{-10} \text{ e.s.u.})^2}{(2)(0.529 \times 10^{-8} \text{ cm})}$$

$$= -2.178 \times 10^{-11} \text{ erg (per atom)}$$

$$= -13.6 \text{ eV (per atom).}$$

Velocity of electron is given by (eq. 3) :

$$v = \frac{nh}{2\pi mr}$$

$$= \frac{(1)(6.626 \times 10^{-27} \text{ erg s})}{(2)(3.14)(9.1090 \times 10^{-28} \text{ g})(0.529 \times 10^{-8} \text{ cm})}$$

$$= 2.186 \times 10^8 \text{ cm s}^{-1}$$

### • 1.3. DUAL NATURE OF MATTER

Einstein (1905) suggested that light has a dual character and behaves both as a particle and as a wave. L. de Broglie (1924) suggested that all material particles in motion such as electrons, protons, neutrons, atoms, molecules etc. have dual character. According to L. de Broglie, any moving electron in the atom is a material particle associated with wave properties and he compared electrons with photons having negligible mass.

According to L. de Broglie, the wavelength  $\lambda$  of a particle of mass  $m$  and velocity  $u$  is given by the relation :

$$\lambda = \frac{h}{mu}$$

where  $h$  is Planck's constant and  $mu$  is the momentum of the particle.

**Derivation of de Broglie's equation :** The relation between the particle nature and wave nature of electron is known as de Broglie equation. According to Planck, the energy of a quantum of radiation is given by :

$$E = h\nu \quad \dots (i)$$

According to Einstein, mass and energy are related as :

$$E = mc^2 \quad \dots (ii)$$

where  $c$  is the velocity of light.

Combining equation (i) and (ii), we have :

$$h\nu = mc^2$$

$$\text{or } \frac{h\nu}{c} = mc$$

$$\text{or } \frac{h}{c/\nu} = mc$$

$$\text{or } \frac{h}{\lambda} = mc$$

$$\text{or } \lambda = \frac{h}{mc}$$

This equation is applicable for photon. According to L. de Broglie, the above equation can also be applied to material particles by substituting the mass of the particle  $m$  and its velocity  $u$  in place of velocity of light  $c$ . Thus, wavelength  $\lambda$  of material particle is given by

$$\lambda = \frac{h}{mu}$$

This relation is known as de Broglie equation.

$$\text{or } \lambda = \frac{h}{p}$$

where  $p$  is the momentum of the particle. This helps in the calculation of wavelength of atom waves.

### • 1.4. WAVE MECHANICAL MODEL

The motion of electron in the atom is not simply mechanical as postulated by Bohr and Sommerfield. The modern theory of the structure of atom is based upon wave mechanics given by L. de Broglie and Schrodinger. According to L. de Broglie, an moving electron in the atom is a material particle associated with wave properties. Instead of moving in a definite orbit, the electrons move in a random manner: sometimes close to the nucleus and sometimes a distance far away from it. It moves in all the directions instead of moving in one plane.

According to Bohr's theory, the electrons move in only those orbitals for which the angular momentum of the moving electron is an integral multiple of  $\frac{h}{2\pi}$  i.e.,

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

De Broglie equation helps to explain the Bohr's postulate of quantisation of angular momentum of an electron. Consider an electron moving around the nucleus in the form of a wave in a circular orbit of radius  $r$ . The electron wave may be continuously in phase or out of phase. If the circumference of the circular orbit is an integral multiple of wavelength, the electron wave is in phase (Fig. 1). But, if the circumference of the circular orbit is not an integral multiple of wavelength, the electron wave will go out of phase (Fig. 2).

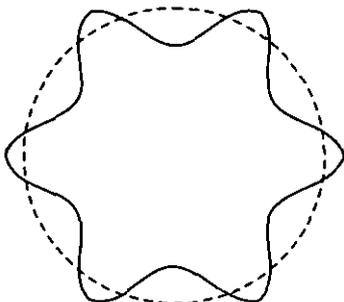


Fig. 1. Wave in phase.

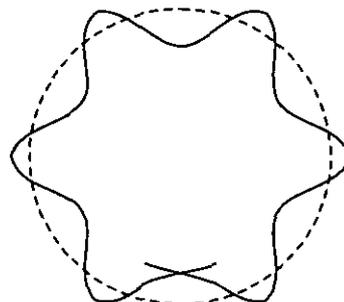


Fig. 2. Wave out of phase.

Thus,

$$\text{Circumference} = n\lambda \quad \text{or} \quad 2\pi r = n\lambda \quad \dots (i)$$

$$\text{But according to de Broglie equation :} \quad \lambda = \frac{h}{mu} \quad \dots (ii)$$

$$\text{From equations (i) and (ii),} \quad 2\pi r = \frac{nh}{mu} \quad \text{or} \quad mvr = \frac{nh}{2\pi}$$

Thus, angular momentum of the moving electron should be an integral multiple of  $\frac{h}{2\pi}$ , or in other words, the angular momentum of the electron is quantised. This is Bohr's postulate which was given without any theoretical basis.

### • 1.5. HEISENBERG'S UNCERTAINTY PRINCIPLE

According to this principle,

***It is impossible to determine simultaneously both the position and the velocity or momentum of a small moving particle like an electron.***

The physical concept of the uncertainty principle may be clear by assuming that all observations have to be made by impact of light radiations or photons. If the object is of a reasonable bigger size, its position or velocity will not be changed by the impact of light photons. So, it will be possible to know both the position and velocity of the object. However, this is not possible when the object is very small, such as an electron. It will suffer a change in its path and velocity due to the impact of even a single photon of light. The path and velocity of an electron, after the impact of light photons, may be quite different from the original path and velocity.

On this basis, Bohr's model in which electrons are considered as particles revolving in definite orbits, *i.e.*, well defined path, does not hold good. However, it will be more correct to say that an electron is associated with a certain energy, *i.e.*, it belongs to a definite energy level and not that it belongs to a definite orbit.

**Uncertainty and concept of probability :** As seen above, it is not possible to know exactly both the position and the momentum of an electron. Thus, certainty of determination of one property introduces uncertainty of determination of the other. The uncertainty in measurement of position,  $\Delta x$ , and the uncertainty of determination of momentum,  $\Delta p$  are related by Heisenberg's relationship as

$$(\Delta x) \times (\Delta p) \geq \frac{h}{4\pi}$$

where  $h$  is Planck's constant.

If  $\Delta x$  is very small, *i.e.*, the position of the electron is known more or less exactly,  $\Delta p$  would be large, *i.e.*, uncertainty with regard to momentum will be large or vice-versa.

**Example 5.** Calculate the uncertainty of velocity of an electron if the uncertainty of its position is  $10^{-10}$  meter. ( $h = 6.6 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}$  and  $m = 9.1 \times 10^{-31} \text{ kg}$ ).

**Solution :** According to Heisenberg's uncertainty principle,

$$(\Delta x) (\Delta u) (m) = \frac{h}{4\pi}$$

$$\begin{aligned} \text{or} \quad \Delta u &= \frac{h}{4\pi (\Delta x) (m)} = \frac{6.6 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}}{(4)(3.14)(10^{-10} \text{ m})(9.1 \times 10^{-31} \text{ kg})} \\ &= 5.7 \times 10^5 \text{ m s}^{-1}. \end{aligned}$$

**Example 6.** Calculate the uncertainty of position of an electron if the uncertainty of its velocity is  $5 \times 10^{15} \text{ ms}^{-1}$ . ( $h = 6.6 \times 10^{-34} \text{ Js}$ ,  $m = 9.1 \times 10^{-31} \text{ kg}$ ).

$$\text{Solution : } \therefore (\Delta x) (\Delta u) (m) = \frac{h}{4\pi}$$

$$\begin{aligned} \therefore (\Delta x) &= \frac{h}{4\pi (\Delta u) (m)} \\ &= \frac{6.6 \times 10^{-34} \text{ Js}}{(4)(3.14)(5 \times 10^5 \text{ ms}^{-1})(9.1 \times 10^{-31} \text{ kg})} \\ &= 1 \times 10^{-10} \text{ m}. \end{aligned}$$

## • 1.6. SCHRODINGER WAVE EQUATION

Starting from de Broglie's concept, Schrodinger developed the theory of wave mechanics and obtained a mathematical equation describing the state of an electron in terms of mass ( $m$ ), total energy ( $E$ ), potential energy ( $V$ ) relative to atomic nucleus, Planck's constant ( $h$ ) and a quantity  $\psi$  called the wavefunction of the electron (or the amplitude of the wave). The equation is called Schrodinger's wave equation. It can be developed from the general differential equation of wave motion in one dimension, *i.e.*, along X-axis.

$$\text{So,} \quad \frac{\partial^2 \psi}{\partial x^2} = -\frac{4\pi^2}{\lambda^2} \psi \quad \dots(11)$$

where  $\lambda$  is the wavelength of light.

From de Broglie's equation,  $\lambda = \frac{h}{mu}$ , thus, from equation (11), we get

$$\begin{aligned} \frac{\partial^2 \psi}{\partial x^2} &= -\frac{4\pi^2}{(h/mu)^2} \psi = -\frac{4\pi^2 m^2 u^2}{h^2} \psi \\ \text{or} \quad \frac{\partial^2 \psi}{\partial x^2} + \frac{4\pi^2 m^2 u^2}{h^2} \psi &= 0 \quad \dots(12) \end{aligned}$$

The total energy ( $E$ ) of a particle (or electron) is given by

$$E = \text{Kinetic energy} + \text{Potential energy}$$

$$\text{or } E = \frac{1}{2} mu^2 + V \quad \text{or } E - V = \frac{1}{2} mu^2$$

$$\text{or } u^2 = \frac{2(E - V)}{m}$$

Putting this value of  $u^2$  in equation (12), we get

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{4\pi^2 m^2}{h^2} \times \frac{2(E - V)}{m} \psi = 0$$

$$\text{or } \frac{\partial^2 \psi}{\partial x^2} + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0 \quad \dots(1)$$

Extending equation (13) to the three dimensions  $x, y$  and  $z$ , we get

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0 \quad \dots(1)$$

Equation (14) is known as *Schrodinger's wave equation*.

**Wave equation and hydrogen atom :** In the case of hydrogen atom in which single electron with charge  $-e$  revolves around a proton with charge  $+e$ , the potential energy,  $V = -(e^2/r)$ , where  $r$  is the distance between the electron and the nucleus

Substituting the value of  $V$  in equation (14), we get

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{h^2} \left[ E - \left( \frac{-e^2}{r} \right) \right] \psi = 0$$

On solving the above equation for  $E$ , we get

$$E = -\frac{2\pi^2 e^4 m}{n^2 h^2} \quad \dots(5)$$

This value of  $E$  is identical with Bohr's value obtained on the basis of classical mechanics introducing arbitrarily the fact that the angular momentum is quantised.

**Significance of wave function,  $\psi$  :** The wave function,  $\psi$  in Schrodinger equation has no physical significance except that it shows the amplitude of the electron wave. The value of  $\psi^2$  gives the probability of finding an electron of a given energy,  $E$  from place to place in a given region around the nucleus.

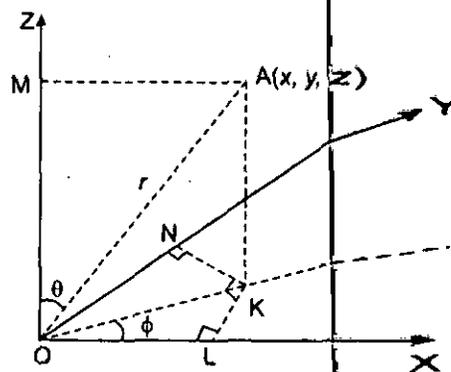
It is possible to identify region of space around the nucleus where there is a high probability of finding an electron associated with a certain energy. The space is known as **atomic orbital**.

It may be noted that in Bohr's theory, the electron associated with a certain energy is supposed to be situated at a certain distance from the nucleus. In wave mechanics, the equation for calculating the exact energy of the electron has been derived, but there is great uncertainty in finding its exact position. This is in conformity with Heisenberg's uncertainty principle.

### Schrodinger Wave Equation in Polar Coordinates

Since it is convenient to solve Schrodinger wave equation in polar coordinates  $r, \theta$  and  $\phi$  in place of cartesian coordinates hence cartesian coordinates are converted into polar coordinates as follows :

Let us consider point  $A$  with coordinates  $x, y, z$  in space shown in figure. In this figure  $AK$  is the perpendicular from  $A$  on  $XY$  plane. While  $KL, KN$  and



Correlation between Cartesian coordinates ( $x, y, z$ ) and polar coordinates ( $r, \theta$  and  $\phi$ ).

$AM$  are the perpendiculars on the axes  $X$ ,  $Y$  and  $Z$  from the points  $K$ ,  $K$  and  $A$  respectively.

Let line  $OA = r$  makes angle  $\theta$  with  $Z$ -axis and line  $OK$  makes angle  $\phi$  with  $X$ -axis. Then according to figure we may write :

$$z = OM = r \cos \theta \text{ and } OK = AM = r \sin \theta$$

$$y = ON = KL = OK \sin \phi = r \sin \theta \sin \phi$$

$$x = OL = OK \cos \phi = r \sin \theta \cos \phi$$

Accordingly in polar coordinates eq. (14) may be written as :

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \Psi(r, \theta, \phi)}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \Psi(r, \theta, \phi)}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \Psi(r, \theta, \phi)}{\partial \phi^2} + \frac{8\pi^2 m}{h^2} \left( E + \frac{e^2}{r} \right) \Psi(r, \theta, \phi) = 0 \quad \dots (15)$$

Note that now  $\Psi$  will be a function of variables  $r$ ,  $\theta$  and  $\phi$  instead of  $x$ ,  $y$  and  $z$ . Therefore we are writing  $\Psi(r, \theta, \phi)$  in place of  $\Psi(x, y, z)$  in the above equation to solve this equation we may write :

$$\Psi(r, \theta, \phi) = R(r) \Theta(\theta) \Phi(\phi)$$

Obviously  $R(r)$  is a function depending on  $r$  and not on  $\theta$  and  $\phi$ . Similarly  $\Theta(\theta)$  is a function depending on  $\theta$  and not on  $r$  and  $\phi$ , similarly  $\Phi(\phi)$  is a function depending on  $\phi$  and not on  $r$  and  $\theta$ .

Here  $R(r)$  is known as the *radial wave function* while the product of other two functions  $\Theta(\theta)$  and  $\Phi(\phi)$  are known as *angular wave functions*.

For the sake of simplicity the above equation is splitted into following three equations as :

$$(1) \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial R(r)}{\partial r} \right) - \frac{\beta}{r^2} R(r) + \frac{8\pi^2 m}{h^2} \left( E + \frac{e^2}{r} \right) R(r) = 0 \quad \dots (16)$$

This equation is a function of  $r$  only and on solution gives  $R(r)$  \*.

$$(2) \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \Theta(\theta)}{\partial \theta} \right) - \frac{m^2 \Theta(\theta)}{\sin^2 \theta} + \beta \Theta(\theta) = 0 \quad \dots (17)$$

This equation is a function of  $\theta$  only and, on solution, gives  $\Theta(\theta)$  \*\*.

$$(3) \frac{\partial^2 \Phi(\phi)}{\partial \phi^2} + m^2 \Phi(\phi) = 0 \quad \dots (18)$$

This equation is a function of  $\phi$  only and, on solution, gives  $\Phi(\phi)$  \*\*.

\* On solving equation (16) following equation is obtained :

$$R(r)_{n, l} = \sqrt{\left( \frac{2Z}{na_0} \right)^3 \frac{(n-l-1)!}{2n (n+l)!}} e^{-\rho/2} \rho^l L_{n+l}^{2l+1}(\rho)$$

where  $\rho = \left( \frac{2Z}{na_0} \right) r$  and  $L_{n+l}^{2l+1}(\rho)$  is the associated Laguerre polynomial. The numbers  $n$  and  $l$  are the two integral quantum numbers described ahead and  $a_0$  is Bohr's radius of hydrogen atom. When  $n = 1$  then  $l = 0$ .

\*\* On solving eqs. (17) and (18) following equations are obtained :

$$\Theta_{l, m}(\theta) = \sqrt{\frac{(2l+1)(l-|m|)!}{2(l+|m|)!}} P_l^m(\cos \theta)$$

and

$$\Phi(\phi) = \frac{1}{\sqrt{2\pi}} e^{\pm im\phi}$$

where  $P_l^m(\cos \theta)$  is the associated Legendre polynomial. Obviously from the expression for  $\Theta(\theta)$  magnetic quantum number is introduced.

Note that the wave function  $R(r)$  gives the energy and size of the orbitals. The angular wave function, the product of  $\Theta(\theta)$  and  $\Phi(\phi)$ , gives the shapes of the orbitals. Both these aspects are discussed here.

### 1. The Radial Wave Function, $R(r)$

The solution of eq. (16) for H,  $\text{He}^+$ ,  $\text{Li}^{2+}$  etc yields two quantum numbers  $n$  and  $l$  which are called as principal quantum numbers ( $n$ ) of Bohr theory and azimuthal quantum number ( $l$ ) of Bohr-Sommerfeld theory. The value of  $l$  depends upon  $n$ , which are 0 to  $(n - 1)$ . For  $l = 0, 1, 2, 3$  these are designated by  $s, p, d, f$  respectively.

Therefore radial wave function is written as  $R_{n,l}(r)$  or simply  $R_{n,l}$  for simplicity. For the electron in  $s$  and  $p$  orbitals radial wave functions are given as follows :

$$R_{1,0}, \text{ i.e., } R_{1s} = 2 \left( \frac{Z}{a_0} \right)^{3/2} e^{-\sigma}$$

Radial wave function of electron in  $1s$  orbital.

$$R_{2,0}, \text{ i.e., } R_{2s} = 2^{-3/2} \left( \frac{Z}{a_0} \right)^{3/2} (2 - \sigma) e^{-\sigma/2}$$

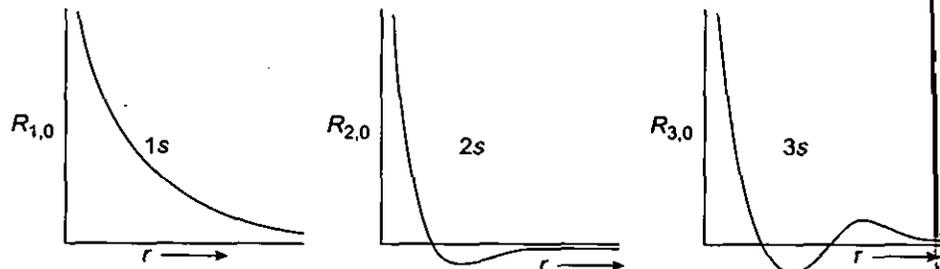
Radial wave function of electron in  $2s$  orbital.

$$R_{2,1}, \text{ i.e., } R_{2p} = 2^{-1} 6^{-1/2} \left( \frac{Z}{a_0} \right)^{3/2} \sigma e^{-\sigma/2}$$

Radial wave function of electron in  $2p$  orbital.

In the above functions,  $a_0$  is Bohr's radius,  $Z$  is the atomic number and  $\sigma$  is  $Zr/a_0$ .

The following types of plots are obtained for  $1s, 2s$  and  $3s$  orbital, when we plot  $R_{n,l}$  against  $r$ ; distance of the electron from the nucleus.

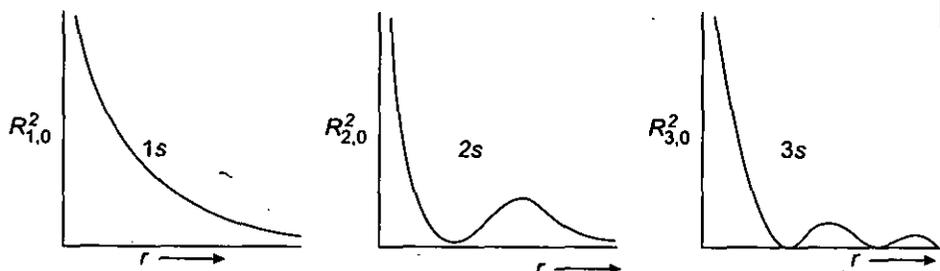


Plots of  $R(r)$  versus  $r$  for electrons belonging to different orbitals.

Evidently  $R_{n,l}$  can not be related with probability density around any point at distance  $r$  from the nucleus. It is due to following two objections :

- (i) The value of  $R_{n,l}$  is maximum at  $r = 0$  i.e., nucleus of the atom, which is not true.
- (ii) For  $2s$  and  $3s$  electrons;  $R_{n,l}$  has both positive and negative values. But the probability density cannot be negative.

The second objection can be removed by considering  $R_{n,l}^2$  to be related to probability density in place of  $R_{n,l}$ . When we plot  $R_{n,l}^2$  against  $r$  following curves are obtained for  $1s, 2s$  and  $3s$  orbitals.



Plot of  $R_{n,l}^2$  versus  $r$  for electron belonging to different orbitals.

No doubt in these cases probability density is not negative but its value is maximum when  $r = 0$ , which is not possible. Therefore we may state that neither  $R_{n,l}$  nor  $R_{n,l}^2$  can be directly related with the probability of finding the electron at a distance  $r$  from the nucleus:

### Radial Probability Distributions Curve

To enquire, how much of the electron is likely to be found at certain distance from the nucleus, we plot a graph between  $\psi^2$  and  $r$  (distance from the nucleus) of the atom.

Such curves are known as probability distribution curve. But in place of such curve we plot radial probability distribution curve which means the probability of finding an electron within the small **radial space** around the nucleus. If  $\psi^2$  is the probability of the electron cloud at

varying distance from  $r$  to  $r + dr$  from the nucleus, then the radial density is defined as the product of  $R_{n,l}^2$  by the volume ( $dV$ ) over which the electron cloud is spreaded. The value of  $dV$  may be calculated as :

$$dV = \frac{4}{3} \pi (r + dr)^3 - \frac{4}{3} \pi r^3$$

$$= \frac{4}{3} \pi [r^3 + 3r^2 dr + 3r dr^2 + dr^3 - r^3] = \frac{4}{3} \pi (3r^2 dr)$$

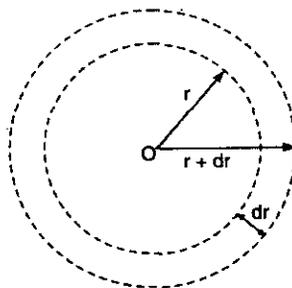
Neglecting  $dr^2$  and  $dr^3$  being a very-very small values.

$$\text{or } dV = 4\pi r^2 dr$$

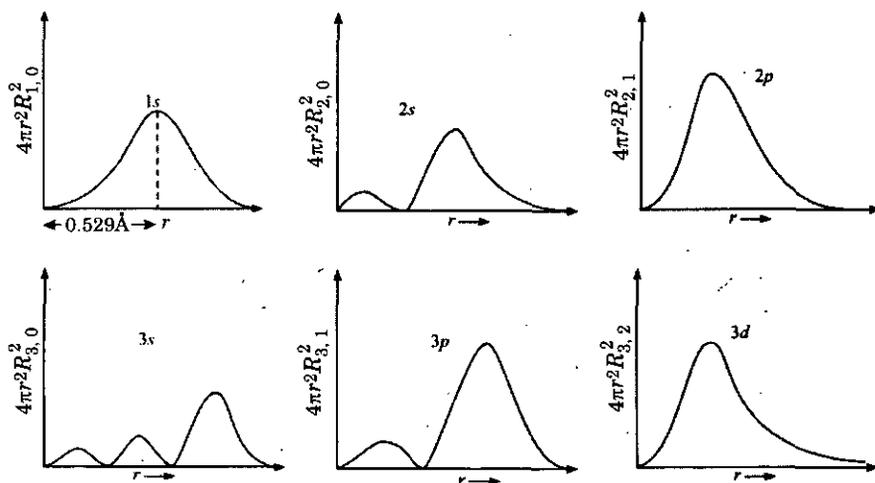
Thus **radial probability** (the probability of finding electron within the thickness  $dr$  around the nucleus) may be given as :

$$D = \rho dV = R_{n,l}^2 \cdot dV = R_{n,l}^2 \cdot 4\pi r^2 dr$$

The **radial probability distribution** may be given as the integration of above term within the range  $r = 0$  to  $r = r$  i.e.,  $\int_0^r R_{n,l}^2 \cdot 4\pi r^2 \cdot dr$ . The curves obtained by plotting  $4\pi r^2 dr \cdot R_{n,l}^2$  against  $r$  are known as radial probability distribution curve or radial charge density curve or simply radial distribution curves. Similar curves are obtained if we consider the complete wave function i.e.,  $\Psi(r, \theta, \phi)$  or  $R(r) \Theta(\theta) \Phi(\phi)$ . It is due to the fact that the expression  $4\pi r^2 dr \cdot R_{n,l}^2$  becomes  $4\pi r^2 \Psi^2(r, \theta, \theta) dr$ . Out of the



Distribution of space around the nucleus



Radial probability distribution for 1s, 2s, 3s, 2p, 3p and 3d orbitals in hydrogen atom.

three components of  $\Psi^2(r, \theta, \phi)$  viz  $R^2(r)$ ,  $\Theta^2(\theta)$  and  $\Phi^2(\phi)$  only  $R^2(r)$  varies with  $r$  while the other two terms *i.e.*,  $\Theta^2(\theta)$  and  $\Phi^2(\phi)$  do not vary with  $r$ . The general shapes of the radial density/radius plots are shown above.

Some important features about these curves are given below :

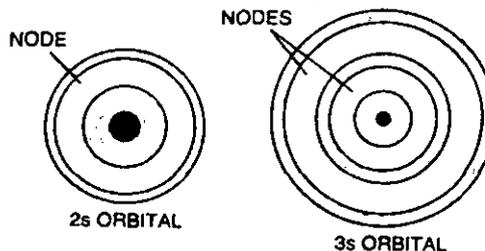
(i) The probability of finding the electron is zero when  $r = 0$  *i.e.* at the origin/nucleus.

(ii) The probability of finding the electron increases with increase of the value of  $r$  as we move from the nucleus. It becomes maximum at a certain value (*e.g.* in the case of  $1s$  orbital it is maximum at  $r = 0.529 \text{ \AA}$ ) and then decreases to zero.

It is very interesting to note that this value is the same as calculated by Bohr's equation.

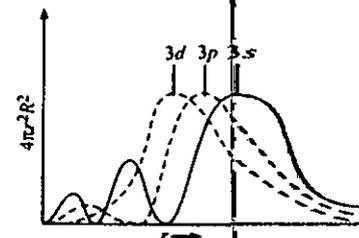
(iii) In the case of  $2s$  electron, the value of  $D$  is zero at  $r = 0$ , this value increases with increase of  $r$  and becomes maximum at  $0.529 \text{ \AA}$  ( $r_0$ ) then it decreases with increase of  $r$  and becomes zero (at  $r = 2 \times r_0$ ). Now the value of  $D$  increases with rise of  $r$  and becomes maximum at  $5r_0$  and finally approaches to zero as  $r$  tends to infinity. This implies that within a spherical orbital of  $2s$ -electron, there is a spherical shell within which the probability of finding the electron is almost zero. This is called a **node** or **nodal plane**.

In the same way in the case of  $3s$ -electron we get two nodal planes and we get three maximum values for  $D$ . The number of radial nodes in an orbital is given by  $n - l - 1$ . In  $n$   $s$ -orbitals there are  $(n - 1)$  nodal planes. Since for  $s$  orbital ( $l = 0$ )  $m$  has only one value ( $m = 0$ ) hence there is only one possible orientation. This means that the value of  $D$  is the same in all directions at a particular distance from the nucleus. Hence  $s$ -orbitals are spherically symmetrical around the nucleus. The shape of  $1s$  orbital is shown here. The shapes of  $2s$  and  $3s$  orbitals are also shown in figure.



Shapes of  $2s$  and  $3s$  orbitals.

(iv) In the case of  $2p$  orbital, it can be seen that the maximum probability is slightly less than that for the  $2s$  orbital. The distance of the maximum probability for the  $2p$ -electron ( $2.645 \text{ \AA}$ ) is slightly larger than that for the  $2s$ -electron ( $2.116 \text{ \AA}$ ), but much larger than that for the  $1s$ -electron ( $0.529 \text{ \AA}$ ). It means that  $2s$ -electron spends more of its time close to the nucleus than does the  $2p$ -electron. Therefore  $2s$ -electron is bound more strongly to the nucleus than the  $2p$ -electron. In other words  $2s$ -electron has lower energy than  $2p$ -electron or we can say that the  $2s$ -electron has lower energy than  $2p$ -electron although both the electrons are of the same principal quantum number.

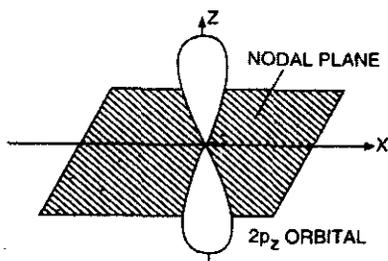


Combined radial probability distribution for  $3s$ ,  $3p$  and  $3d$  orbitals

For  $p$  orbital ( $l = 1$ ) there are three values for  $m$ , *i.e.*,  $-1, 0, +1$  which show three orientations for  $p$  orbitals and are named as  $p_x, p_y$  and  $p_z$  with subscripts  $x, y$  and  $z$  referring to the coordinate axes along which their maximum electron density lie. In the absence of magnetic field these three  $p$  orbitals are equivalent in energy and called triply degenerate or three-fold degenerate. But in the presence of magnetic field, the relative energies of the  $p$ -orbitals vary and depend upon their orientation. Due to this fact, fine structure is observed.

Each  $p$ -orbital has two lobes symmetrical about a particular axis. These two lobes (dumb-bell shape) touch each other at the origin where there is zero electron density. This plane is called **nodal plane**,  $p_z$  orbital is shown in fig. Similarly  $p_x$  and  $p_y$  orbitals may be shown.

(v) In the case of  $3p$  orbital we get two maxima. The smaller additional peak corresponds to  $2p$ -orbital and the other corresponds to  $3p$ -orbital. In the case of



Shape of  $2p_z$  orbital

$3d$ -orbital we get only one peak. The order of distance for the maximum probability for  $3s$ ,  $3p$  and  $3d$  is in the order of  $3s > 3p > 3d$  orbital that this difference is slightly larger while the difference between corresponding 2nd and 1st quantum number is much larger. It means  $3s$ -electron spends more of its time close to the nucleus than does the  $3p$ -electron and  $3d$ -electron. Therefore  $3s$ -electron is bound more strongly to the nucleus than the  $3p$ -electron and  $3p$  electron is bound more strongly to the nucleus than  $3d$ -electron. In other words the order of stability of these orbitals is  $3s > 3p > 3d$  or we can say that order of their energy level is  $3s < 3p < 3d$  although all the three electrons are of the same principal quantum number.

For  $d$ -orbital ( $l = 2$ ) there are five values for  $m$  i.e.,  $-2, -1, 0, +1, +2$  which show five orientations for  $d$ -orbitals and named as  $dxy, dyz, dz^2, dxz, dx^2 - y^2$  respectively. In the absence of magnetic field these five  $d$ -orbitals are equivalent in energy and called **five-fold degenerate**. But in the presence of magnetic field, the relative energies of the  $d$ -orbitals vary and depend upon their orientation.

## 2. The Angular Wave Function, $\Theta(\theta) \cdot \Phi(\phi)$

The solution of eqs. (17) and (18) yield a new quantum number which is called magnetic quantum number and represented by ' $m$ '. Its values depend upon azimuthal quantum number ' $l$ ' and values can be  $\pm l$  or we may write as  $0, \pm 1, \pm 2, \dots, \pm l$ . Thus total values are  $(2l + 1)$ .

As discussed above the angular wave function is the product of  $\Theta(\theta)$  and  $\Phi(\phi)$ . But the wave function  $\Theta(\theta)$  is generally written as  $\Theta_{l, m}(\theta)$  or simply as  $\Theta_{l, m}$ . As well as the wave function  $\Phi_m(\phi)$  is written as  $\Phi_m$ . Thus,

$$\text{Angular wave function} = \Theta_{l, m} \Phi_m \quad \dots (19)$$

Since complete wave function  $\Psi(r, \theta, \phi)$  is the product of the radial wave function ( $R_{n, l}$ ) and the angular wave function  $\Theta_{l, m} \Phi_m$  hence we may write,

$$\Psi(r, \theta, \phi) = R_{n, l} \Theta_{l, m} \Phi_m$$

**Angular Wave Functions and Shapes of the Orbitals :** The wave functions  $\Theta_{l, m}$  and  $\Phi_m$  for different values of  $l$  ( $0, 1, 2, \dots$ ) and  $m$  ( $0, \pm 1, \pm 2, \dots$ ) for the hydrogen atom are given below :

$$\Theta_{0, 0} = \frac{\Theta_{l, m}}{\sqrt{2}} = \frac{1}{\sqrt{2}}$$

$$\Theta_{1, 0} = \sqrt{\frac{3}{2}} \cos \theta$$

$$\Phi_0 = \frac{\Phi_m}{\sqrt{2\pi}} e^0 = \frac{1}{\sqrt{2\pi}}$$

$$\Phi_{+1} = \frac{1}{\sqrt{2\pi}} e^{+i\phi} = \frac{1}{\sqrt{2\pi}} (\cos \phi + i \sin \phi)$$

$$\begin{aligned} \Theta_{1, \pm 1} &= \sqrt{\frac{3}{4}} \sin \theta & \Phi_{-1} &= \frac{1}{\sqrt{2\pi}} e^{-i\phi} = \frac{1}{\sqrt{2\pi}} (\cos \phi - i \sin \phi) \\ \Theta_{2, 0} &= \sqrt{\frac{5}{8}} (3 \cos^2 \theta - 1) & \Phi_{+2} &= \frac{1}{\sqrt{2\pi}} e^{+2i\phi} = \frac{1}{\sqrt{2\pi}} (\cos 2\phi + i \sin 2\phi) \\ \Theta_{2, \pm 1} &= \frac{\sqrt{15}}{2} (\sin \theta \cos \theta) & \Phi_{-2} &= \frac{1}{\sqrt{2\pi}} e^{-2i\phi} = \frac{1}{\sqrt{2\pi}} (\cos 2\phi - i \sin 2\phi) \\ \Theta_{2, \pm 2} &= \frac{\sqrt{15}}{4} (\sin^2 \theta) \end{aligned}$$

As discussed above the radial wave function and angular wave function give the size and shape of the orbitals respectively. Obviously complete wave function *i.e.*, product of radial and angular wave functions give the size and shape of the orbitals. With the help of complete wave function, now we deduce the shape of the orbitals.

**Shapes of s orbitals :** Since for a *ns* orbital  $l = 0$  and  $m = 0$  hence the complete wave function is written as follows :

$$R_{n, 0}(r) \Theta_{0, 0} \Phi_0 = R_{n, 0}(r) \frac{1}{\sqrt{2}} \times \frac{1}{\sqrt{2\pi}} = R_{n, 0}(r) \frac{1}{2\sqrt{\pi}} \quad \dots (20)$$

Evidently the eq. (20) is independent of the angles  $\theta$  and  $\phi$ , therefore, the orbital is spherical and symmetrical along all directions for a particular value of  $r$ , *i.e.*, it has a spherical shape. The 1s orbital has no radial node, on the other hand 2s and 3s orbitals have one and two nodes respectively as shown on page 14.

**Shapes of p orbitals :** Since for *p*-orbitals  $l = 1$  and  $m = 0, +1$  and  $-1$  hence the complete wave function can be written as follows :

$$R_{n, 1}(r) \Theta_{1, 0} \Phi_0 = R_{n, 1}(r) \sqrt{\frac{3}{2}} \cos \theta \times \frac{1}{\sqrt{2\pi}} = R_{n, 1}(r) \sqrt{\frac{3}{4\pi}} \cos \theta \quad \dots (21)$$

$$R_{n, 1}(r) \Theta_{1, +1} \Phi_{+1} = R_{n, 1}(r) \sqrt{\frac{3}{4}} \sin \theta \times \frac{1}{\sqrt{2\pi}} e^{+i\phi} \quad \dots (22)$$

$$R_{n, 1}(r) \Theta_{1, -1} \Phi_{-1} = R_{n, 1}(r) \sqrt{\frac{3}{4}} \sin \theta \times \frac{1}{\sqrt{2\pi}} e^{-i\phi} \quad \dots (23)$$

Out of these eqs. (21), (22) and (23) only eq. (21) is real while eqs. (22) and (23) are imaginary because a term 'i' is involved in these two equations. To get the real wave functions for *p* orbitals, two linear combination of angular wave functions represented by eqs. (22) and (23) are taken into consideration. Thus we get two normalized linear combinations which may be represented as :

$$(i) \frac{1}{\sqrt{2}} R_{n, 1}(r) (\Theta_{1, +1} \Phi_{+1} + \Theta_{1, -1} \Phi_{-1})$$

$$(ii) \frac{1}{\sqrt{2}} R_{n, 1}(r) (\Theta_{1, +1} \Phi_{+1} - \Theta_{1, -1} \Phi_{-1})$$

These wave functions yield two results which may be represented as :

$$\text{Combination 1 for real } p \text{ wave function} = R_{n, 1}(r) \sqrt{\frac{3}{4\pi}} \sin \theta \cos \phi \quad \dots (24)$$

$$\text{Combination 2 for real } p \text{ wave function} = R_{n, 1}(r) \sqrt{\frac{3}{4\pi}} \sin \theta \sin \phi \quad \dots (25)$$

Thus, eqs. 21, 24 and 25 now represent a set of real wave functions for *p* orbitals with  $l = 1$  and  $m = 0, +1, -1$ .

Now we get a set of real wave functions for *p* orbitals (with quantum numbers  $l = 1$  and  $m = 0, +1, -1$ ) according to eq. (21), (24) and (25).

On the basis of above discussion the shapes of the  $2p$  orbitals are represented by the real wave function as given by eqs. (21), (24) and (25). Now we express these three functions in terms of the cartesian coordinates. Accordingly for  $2p$  orbital eq. (21) may be written as :

$$R_{2,1}(r)\sqrt{\frac{3}{4\pi}}\cos\theta \quad \text{or} \quad R_{2,1}(r)\sqrt{\frac{3}{4\pi}}\times\frac{z}{r} \quad \dots (26)$$

Because  $z = r \cos \theta$

Since it is a function of  $z$  hence  $p$ -orbital is known as  $p_z$  wave function. When it is plotted in three dimensional space we get dumb-bell shape as shown in the figure. According to eq. (26)  $p_z$  will be positive when  $z$  is positive and will be negative when  $z$  is negative. Therefore in figure positive and negative signs are given. These are simply geometric signs of the plotted wave functions. One should not be confused with positive and negative charge.

Now we consider real wave function as given by eq. (24). As discussed above we get second real angular  $p$  wave function eq. (24) which may be given as :

$$R_{2,1}(r)\sqrt{\frac{3}{4\pi}}\sin\theta\cos\phi$$

or 
$$R_{2,1}(r)\sqrt{\frac{3}{4\pi}}\times\frac{x}{r} \quad \dots (27)$$

(See figure on page 10)

Since it is a function of  $x$  hence  $p$ orbital is known as  $p_x$  wave function. When it is plotted in three dimensional space we again get dumb-bell shape as shown in the figure. The sign of wave function may be explained as above.

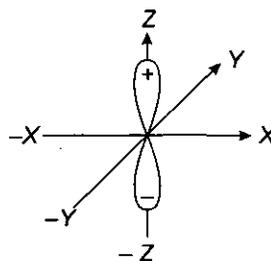
In the same way the real wave functions as given in eq. (25) we may write.

The third real  $p$  wave function for combination 2

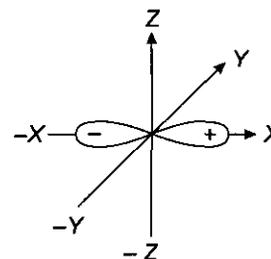
$$\begin{aligned} &= R_{2,1}(r)\sqrt{\frac{3}{4\pi}}\sin\theta\sin\phi \\ &= R_{2,1}(r)\sqrt{\frac{3}{4\pi}}\times\frac{y}{r} \quad \dots (28) \end{aligned}$$

Since it is function of  $y$  hence  $p$ orbital is known as  $p_y$  wave function other things are as above.

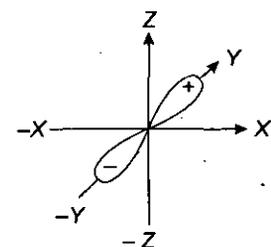
Thus it is concluded that  $p$ -orbitals have dumb-bell shape. But the space occupied by  $2p$ ,  $3p$  and  $4p$  will be in  $2p < 3p < 4p$  order. Since radial nodes are given as  $(n - l - 1)$  hence  $2p$ ,  $3p$  and  $4p$  orbitals have zero, one and two radial node respectively. These orbitals may be represented as :



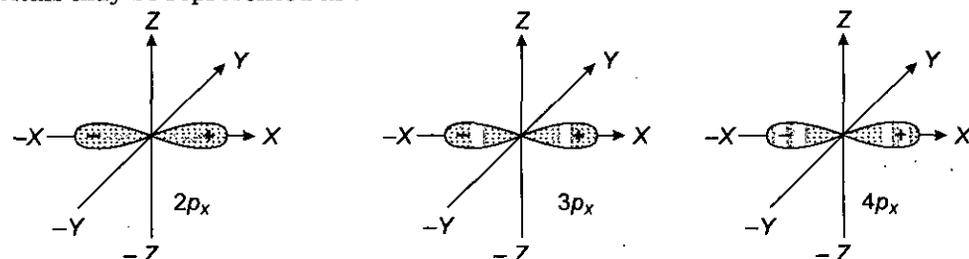
The shape of  $p_z$  orbital



The shape of  $p_x$  orbital



The shape of  $p_y$  orbital



The exact shapes of  $2p_x$ ,  $3p_x$  and  $4p_x$  orbitals.

**Shapes of d orbitals :** We know that for d orbitals,  $l = 2$  and  $m = 0, +1, +2, -1, -2$ . The complete wave functions for the d orbitals of principal quantum number ( $n$ ) written as follows :

$$R_{n,2}(r) \Theta_{2,0} \Phi_0 = R_{n,2}(r) \sqrt{\frac{5}{16\pi}} (3 \cos^2 \theta - 1) \quad \dots (2)$$

$$R_{n,2}(r) \Theta_{2,+1} \Phi_{+1} = R_{n,2}(r) \sqrt{\frac{15}{8\pi}} (\sin \theta \cos \theta) e^{i\phi} \quad \dots (30)$$

$$R_{n,2}(r) \Theta_{2,+2} \Phi_{+2} = R_{n,2}(r) \sqrt{\frac{15}{32\pi}} (\sin^2 \theta) e^{i2\phi} \quad \dots (31)$$

$$R_{n,2}(r) \Theta_{2,-1} \Phi_{-1} = R_{n,2}(r) \sqrt{\frac{15}{8\pi}} (\sin \theta \cos \theta) e^{-i\phi} \quad \dots (32)$$

$$R_{n,2}(r) \Theta_{2,-2} \Phi_{-2} = R_{n,2}(r) \sqrt{\frac{15}{32\pi}} (\sin^2 \theta) e^{-i2\phi} \quad \dots (33)$$

Out of these five equations only eq. (29) is real equation while other four equations are imaginary because term  $i$  is involved for d orbital. As in the case of p-orbitals wave functions, here real d-orbital wave functions are obtained from eqs. (30) and (32) as follows :

$$(i) \quad 1/\sqrt{2} R_{n,2}(r) (\Theta_{2,+1} \Phi_{+1} + \Theta_{2,-1} \Phi_{-1})$$

$$(ii) \quad 1/\sqrt{2} R_{n,2}(r) (\Theta_{2,+1} \Phi_{+1} - \Theta_{2,-1} \Phi_{-1})$$

Similarly from eqs. (31) and (33) are as follows :

$$(i) \quad 1/\sqrt{2} R_{n,2}(r) (\Theta_{2,+2} \Phi_{+2} + \Theta_{2,-2} \Phi_{-2})$$

$$(ii) \quad 1/\sqrt{2} R_{n,2}(r) (\Theta_{2,+2} \Phi_{+2} - \Theta_{2,-2} \Phi_{-2})$$

Thus we get five real d orbital wave functions as follows :

(A) Real d wave function (1) derived from eq. (29)

$$= R_{n,2}(r) \sqrt{\frac{5}{16\pi}} (3 \cos^2 \theta - 1) \quad \dots (34)$$

$$\text{or} \quad = R_{n,2}(r) \sqrt{\frac{15}{16\pi}} (3z^2 - r^2) \times \frac{1}{r^2} \quad \dots (35)$$

Since this d wave function varies as  $z^2$  hence it is called  $dz^2$  wave function.

(B) Real d wave function (2) derived from linear combination (i) of eqs. (30) and (32)

$$= R_{n,2}(r) \sqrt{\frac{15}{4\pi}} \sin \theta \cos \phi \cos \theta \quad \dots (36)$$

$$\text{or} \quad = R_{n,2}(r) \sqrt{\frac{15}{4\pi}} \times \frac{xz}{r^2} \quad \dots (37)$$

Since this d wave function varies as  $xz$  hence it is called  $dxz$  wave function.

(C) Real d wave function (3) derived from linear combination (ii) of eqs. (30) and (32)

$$= R_{n,2}(r) \sqrt{\frac{15}{4\pi}} \sin \theta \sin \phi \cos \theta \quad \dots (38)$$

$$\text{or} \quad = R_{n,2}(r) \sqrt{\frac{15}{4\pi}} \times \frac{yz}{r^2} \quad \dots (39)$$

As discussed above the d wave function is called  $d_{yz}$  wave function.

(D) Real d wave function (4) derived from linear combination (i) of eqs. (31) and (33).

$$= R_{n,2}(r) \sqrt{\frac{15}{16\pi}} \sin^2 \theta \cos 2\phi \quad \dots (40)$$

$$\begin{aligned}
 &= R_{n,2}(r) \sqrt{\frac{15}{16\pi}} \sin^2 \theta (\cos^2 \phi - \sin^2 \phi) \\
 &= R_{n,2}(r) \sqrt{\frac{15}{16\pi}} \sin^2 \theta \cos^2 \phi - \sin^2 \theta \sin^2 \phi \\
 &= R_{n,2}(r) \sqrt{\frac{15}{16\pi}} \frac{(x^2 - y^2)}{r^2} \quad \dots (41)
 \end{aligned}$$

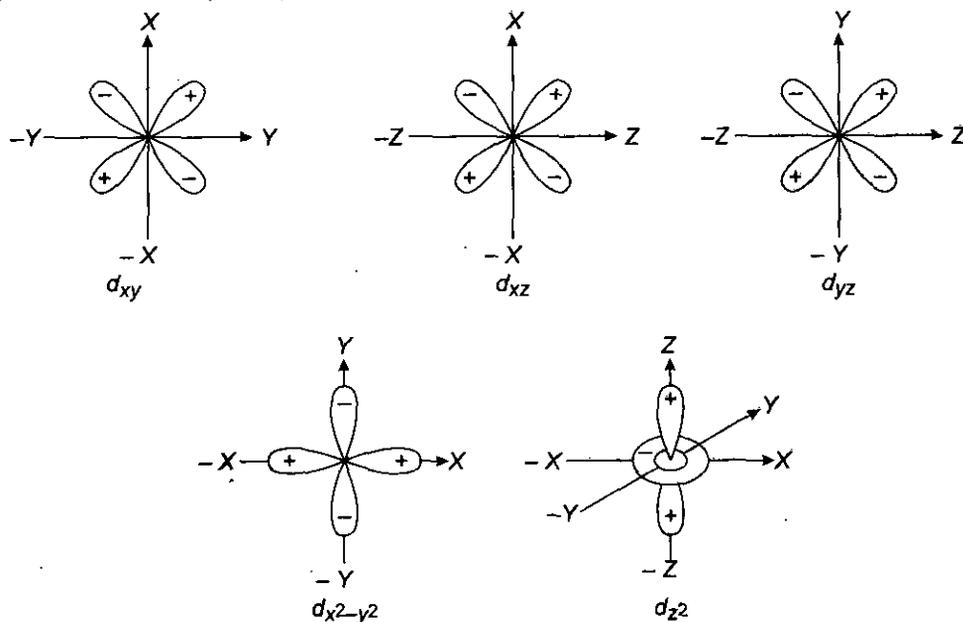
Obviously the  $d$  wave function varies as  $x^2 - y^2$  therefore it is called  $d_{x^2-y^2}$  wave function

(E) Real  $d$  wave function (5) derived from linear combination (ii) of eqs. (31) and (33).

$$\begin{aligned}
 &= R_{n,2}(r) \sqrt{\frac{15}{16\pi}} \sin^2 \theta \sin 2\phi \quad \dots (42) \\
 &= R_{n,2}(r) \sqrt{\frac{15}{16\pi}} \sin^2 \theta 2 \sin \phi \cos \phi \\
 &= R_{n,2}(r) \sqrt{\frac{15}{4\pi}} \sin \theta \cos \phi \sin \theta \sin \phi \\
 &= R_{n,2}(r) \sqrt{\frac{15}{4\pi}} \frac{xy}{r^2} \quad \dots (43)
 \end{aligned}$$

Obviously the  $d$  wave function is called  $d_{xy}$  wave function.

Thus we have five real wave functions of  $d$ -orbitals which are  $d_{z^2}$ ,  $d_{xz}$ ,  $d_{yz}$ ,  $d_{x^2-y^2}$  and  $d_{xy}$ . When these wave function are plotted in three dimensional space yield curves as show below. All these curves are solid curves *i.e.*, three dimensional because of their dependence on  $r = (\sqrt{x^2 + y^2 + z^2})$ .



Shapes of  $d$  orbitals

The sign of the wave functions may be explained as follows :

The shape of  $d_{z^2}$  orbital is dumb-bell shaped curve symmetric about the  $Z$ -axis with a ring-like collar in  $XY$  plane. Here dumb-bell shaped part of the curve has *positive geometric sign*. It is due to the fact square of positive and negative is always positive, while collar has *negative geometric sign*.

The shape of  $d_{xy}$  orbital is double dumb-bell on XY plane. The quantity  $xy$  is positive when both  $x$  and  $y$  are positive or negative. The quantity  $xy$  is negative when one of them ( $x$  or  $y$ ) is negative. The same is the case with  $d_{yz}$  and  $d_{zx}$  orbitals.

The shape of  $d_{x^2-y^2}$  orbital is also double dumb-bell on X and Y axes. In this case the lobes on X-axis will be always positive whether  $x$  is positive or negative. But the lobes on Y-axis will be always negative whether  $y$  is positive or negative.  $-y^2$  will be negative. As discussed for  $p$ -orbitals, the space occupied by  $3d$ ,  $4d$  and  $5d$  will be in the order  $3d < 4d < 5d$ . Since radial nodes are given as  $(n - l - 1)$  hence  $3d$ ,  $4d$  and  $5d$  orbitals have zero, one and two radial nodes respectively. In figure it may be represented as  $p$ -orbitals.

The shapes of  $f$ -orbitals are shown below without any description.

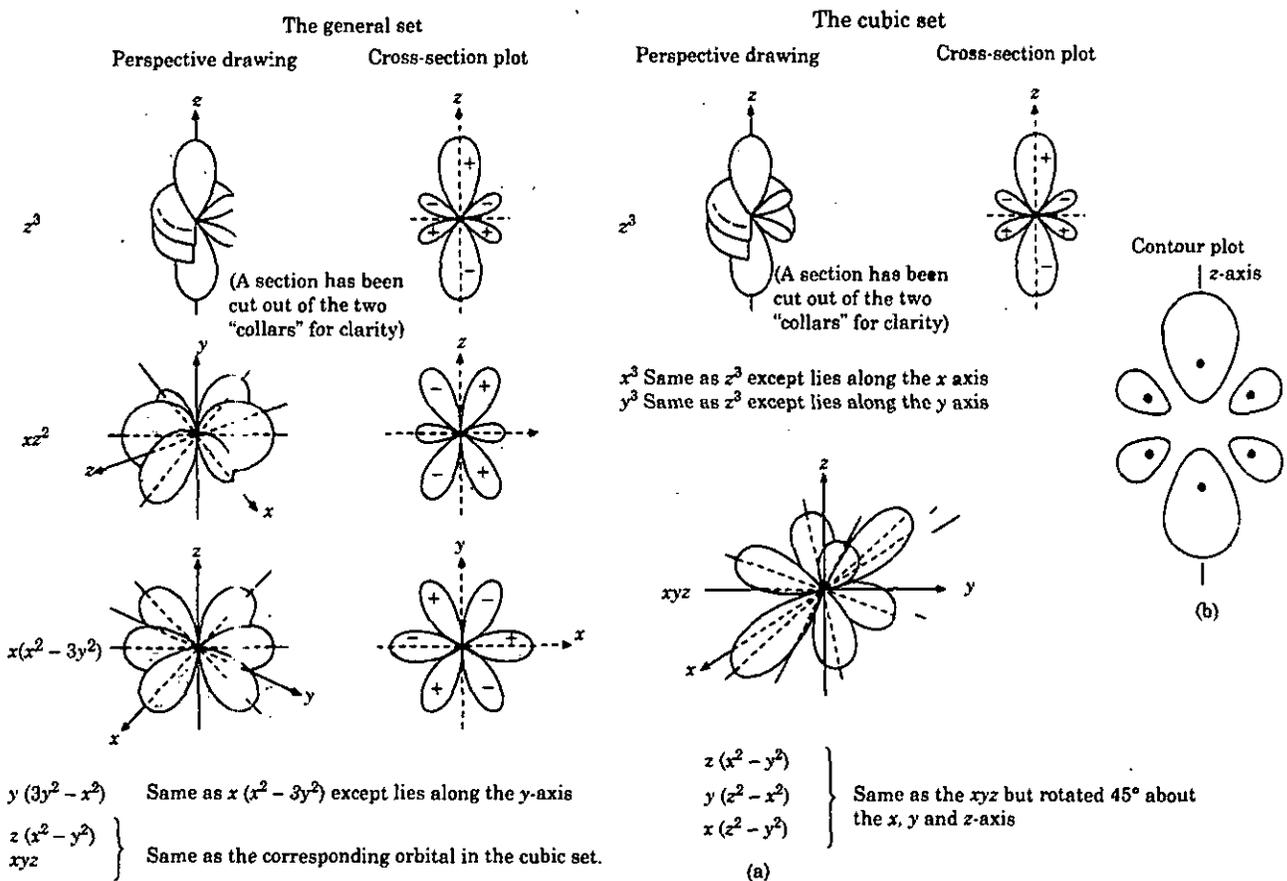


Fig. The  $f$  orbitals : (a) plots of the angular part of the wave functions of the  $f$  orbital; (b) contours of a  $4f$  orbital. Dots indicate maxima in electron density. The lines are drawn for densities which are 10% of Maximum.

## Significance of $\psi$ and $\psi^2$

In Schrodinger's wave equation  $\psi$  represents the amplitude of the spherical wave. According to the theory of propagation of light and sound waves, the square of the amplitude of the wave is proportional to the intensity of light. A similar concept to clarify the requirements of uncertainty principle has been developed for the physical interpretation of wave function,  $\psi$ . This may be stated as the probability of finding an electron in an extremely small volume around a point is proportional to the square of the function  $\psi^2$  at that point.

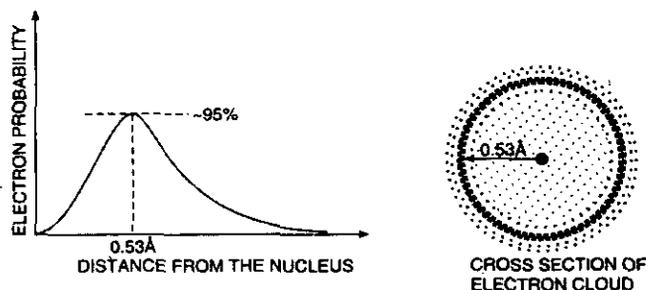
The wave function  $\psi$ , in Schrodinger equation has no physical significance except that it shows the amplitude of the electron wave. However,  $\psi^2$  gives the probability of finding an electron of a given energy, from place to place in a region around the nucleus.

It is possible to identify the region of space around the nucleus where there is maximum probability of finding an electron with a definite energy. This space is known as atomic orbital.

## Atomic Orbitals

One of the important results of the wave mechanical picture is that an electron, while going round the nucleus is constantly oscillating in and out from the nucleus. The region of space swept out by the hydrogen electron represents the size of the hydrogen atom. Hence, the probability of finding the electron in different directions and at different distances from the nucleus can easily be considered. The probability distribution is spherically symmetrical.

The atomic orbital represents a definite region in three dimensional space around a nucleus where there is a high probability of finding an electron, orbital can be defined in another way also. The thin shell like region is space for which electron probability has a high value is known in wave mechanics as an orbital.



Electron probability in hydrogen atom

With high and low electron density space region around the nucleus, the picture of electron probability is generally called as electron being diffused or smeared out as shown here. It is also described as the electron existing as an electron charge cloud. The density of cloud at any point is proportional to  $\psi^2$ , whereas according to wave equation a moving particle is represented by a wave function  $\psi$ .

## Differences between orbit and orbital

(a) Orbit is a definite circular path around the nucleus in which an electron revolves. Orbital is a three-dimensional region around the nucleus within which there is maximum probability of finding the electron having certain energy.

(b) Orbit specifies a definite trajectory of an electron in the atom *e.g.*, in hydrogen atom the electron will always be at a distance  $0.53 \text{ \AA}$  from the nucleus. Orbital does not specify a definite trajectory of an electron in the atom.

(c) Orbit does not follow uncertainty principle while orbital follows.

## Sub-shell or Sub-orbit

In an atom each orbit consists one or more sub-orbits, which have some difference in energy level. These sub-orbits are also known as sub-energy levels for such stationary

states. These are represented by *s*, *p*, *d* and *f* letters which are derived from the characteristics of spectral lines as sharp (*s*), principal (*p*), diffuse (*d*) and fundamental (*f*).

The order of energy levels of these sub-orbits are represented ahead (page 29).

The number of sub-orbits is equal to the orbit number in an atom. The sub-orbits of different orbits are given in the following table.

Orbit	Number of orbit	Total number of sub-orbits in an orbit	Symbols of sub-orbits in an orbit
K	$n = 1$	1	1s
L	$n = 2$	2	2s 2p
M	$n = 3$	3	3s 3p 3d
N	$n = 4$	4	4s 4p 4d 4f

The maximum number of electrons in first orbit (*K*-shell) may be 2. It consists only one sub-orbit i.e., *s*-sub-orbit which can possess maximum 2 electrons. Second orbit (L-shell) can possess maximum 8 electrons. It consists two sub-orbits i.e., *s* and *p* but *s*-sub orbit can possess maximum 2 electrons hence *p*-sub orbit can possess maximum 6 electrons. Similarly we can say *d*-sub-orbits and *f*-sub-orbits can possess maximum 10 and 14 electrons respectively.

Thus different sub-orbits can possess maximum number of electrons as:

Sub-orbit	Maximum number of electrons	Method of representation
<i>s</i>	2	$s^2$
<i>p</i>	6	$p^6$
<i>d</i>	10	$d^{10}$
<i>f</i>	14	$f^{14}$

### • 1.7. QUANTUM NUMBERS

It has been found that in Bohr's theory quantum numbers were introduced as a matter of necessity to fit the theory with experimental data. In Schrodinger wave equation, such numbers come out in natural way through mathematics in solving the equation. These number specify the location and energy of electrons in an atom. Each electron is characterized by four quantum numbers, the Principal, Azimuthal, Magnetic and Spin quantum numbers. Each quantum number is associated with a particular characteristics of electron which it describes.

(i) **Principal quantum number (*n*)** : The Principal quantum number defines an energy shell in an atom where one or more orbitals of the same energy may lie. The different orbitals of same energy are grouped together as degenerate orbitals. It specifies the location and energy of an electron and is measure of the effective volume of the electron cloud. The shells corresponding to  $n = 1, 2, 3, 4$  are denoted by *K, L, M, N* shells respectively. As the distance of the electron from the nucleus increases, its energy becomes higher and higher. This is also known as major energy level. This quantum number represents the size of the orbit. The maximum number of electrons present in any orbit is according to  $2n^2$ .

(ii) **Azimuthal quantum number (*l*)** : This is also known as angular subsidiary or second quantum number. It determines the orbital angular momentum and the shape of the orbital (electron cloud) i.e., whether the cloud is spherical, dumb-bell shaped or of some complicated shape.

This quantum number is represented by ' $l$ '. It represents sub-shell or sub-energy level. Its values depend upon ' $n$ ' and values are 0 to  $(n - 1)$  i.e.,  $l = 0, 1, 2, 3 \dots (n - 1)$ .

If,  $n = 1, l = 0$ ; It is represented by  $1s$ .

$n = 2, l = 0, 1$ ; These are represented by  $2s, 2p$  respectively.

$n = 3, l = 0, 1, 2$ ; These are represented by  $3s, 3p, 3d$  respectively.

$n = 4, l = 0, 1, 2, 3$ ; These are represented by  $4s, 4p, 4d, 4f$  respectively.

If  $l = 0$  then the angular momentum of the electron is zero. It is circular in shape. If  $l = 1, 2$  and  $3$  then the sub orbits are represented by  $p, d$  and  $f$  respectively and shapes are elliptical. The ellipticity increases from  $p$  to  $f$  subshell. The order of energy of these sub-shells is  $f > d > p > s$ . The maximum number of electrons in any sub-shell is according to  $2(2l + 1)$ . This may be represented as in the following table.

Principal Q. No. ( $n$ )	Azimuthal Q. No. ( $l$ )	Sub-shell	Maximum number of electrons as $2(2l + 1)$
4	0	$s$	$2(2 \times 0 + 1) = 2$
	1	$p$	$2(2 \times 1 + 1) = 6$
	2	$d$	$2(2 \times 2 + 1) = 10$
	3	$f$	$2(2 \times 3 + 1) = 14$

(iii) **Magnetic quantum number ( $m$ )** : It describes the orientation of sub-shells in space particularly under the influence of an applied magnetic field.

Actually this quantum number has been introduced to account for the splitting of each spectral line into a number of component lines when a strong magnetic field is applied. This phenomenon is known as **Zeeman effect**. There is also a splitting of spectral lines by an electric field which is known as **Stark effect**. It indicates that sublevel exists as a number of closely related levels which are revealed only in a magnetic field.

The various values of  $m$  for a given value of  $l$  are  $-l, (-l + 1) \dots, 0, 1, 2, \dots, +l$  i.e. the total values are  $(2l + 1)$ . When  $l = 0$ ,  $m$  has only one value i.e. 0; when  $l = 1$ ,  $m$  has three values i.e.  $-1, 0$  and  $+1$ . Hence it follows that for  $s$  orbital ( $l = 0$ ), has only one orientation; for  $p$ -orbital, ( $l = 1$ ), has three orientations,  $d$ -orbital, ( $l = 2$ ), has five orientations and for  $f$ -orbital ( $l = 3$ ) has seven orientations.

$$l = 0; m = 0 \quad (1 \text{ value})$$

$$l = 1; m = -1, 0, +1 \quad (3 \text{ values})$$

$$l = 2; m = -2, -1, 0, +1, +2 \quad (5 \text{ values})$$

$$l = 3; m = -3, -2, -1, 0, +1, +2, +3 \quad (7 \text{ values})$$

Thus  $s$ -suborbit exhibits only one orbital, which is spherical,  $p$ -sub shell exhibits three orbitals ( $p_x, p_y$  and  $p_z$ ), which are oriented on  $x, y$  and  $z$ -axis. The shape of each  $p$ -orbital is **dumb-bell** as shown on page 17. The two lobes of the orbital are separated by a plane having zero electron density. This plane is called **nodal plane**. It is important to note that the probability of finding electron in a particular  $p$ -orbital is equal in both the lobes.

For  $d$ -orbitals ( $l = 2$ ),  $m$  can have five values i.e.,  $-2, -1, 0, +1$  and  $+2$ . Thus there are five orientations in a  $d$ -subshell. The shapes of five  $d$ -orbitals shown on page 19.

It is clear from these figures that there are two sets of  $d$ -orbitals having two different types of orientation in space. The first consists which are designated as  $d_{xy}, d_{xz}$  and  $d_{yz}$ . These have their probability maxima in between the co-ordinate

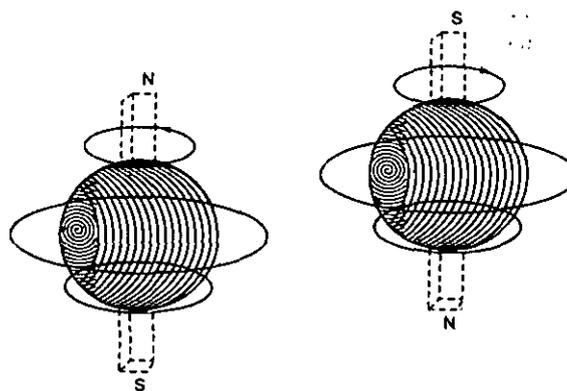
axes. However, the second set consists of two orbitals. Among these one orbital is oriented in the  $XY$ -plane and has maximum probability on  $X$  and  $Y$ -axes. This is designated as  $d_{x^2-y^2}$  orbital. The other orbital is dumb-bell shaped which is oriented along the  $Z$ -axis and is designated as  $d_{z^2}$  orbital. This orbital also has a doughnut-shaped ring of high electron density around the nucleus. It indicates that  $d_{z^2}$  orbital does not have zero electron probability along any axis.

For  $f$ -orbitals ( $l = 3$ )  $m$  can have seven values i.e.  $-3, -2, -1, 0, +1, +2$  and  $+3$ . Thus there are seven orientations in a  $f$ -subshell. The shapes of seven  $f$ -orbitals are shown in figure on page 20.

The figure shown on page 20 presents two sets (i) a "general set" and (ii) "cubic set". The cubic set is advantageous in considering the properties of the orbitals in cubic field (i.e. tetrahedral and octahedral fields).

(iv) Spin quantum number ( $s$ ) : It describes the fourth degree of freedom of the electron and explains the fine structure of spectral lines within atomic levels. The electron in the atom rotates not only around the nucleus but around its own axis as well and two opposite directions of rotation are possible. This rotation of the electron called the spin, gives rise to another quantum number known as spin quantum number. It also indicates the direction in which the electron is spinning, clockwise or anticlockwise. As a convention, the clockwise spin is represented by an arrow ( $\uparrow$ ) pointing upwards while anticlockwise spin is represented by an arrow ( $\downarrow$ ) pointing downwards, there are only two possible values for this quantum number and for electrons these are  $+\frac{1}{2}$  and  $-\frac{1}{2}$  according to the direction of a spin being clockwise and anticlockwise respectively. Mathematically, this quantum number is related by the equation.

$$mvr = \frac{h\sqrt{[s(s+1)]}}{2\pi}$$



Spinning electron

where  $\sqrt{[s(s+1)]} \frac{h}{2\pi}$  = spin angular momentum

$s$  = Absolute magnitude of spin quantum number  
(irrespective of the sign i.e.  $1/2$ )

$m$  = mass of electron

$v$  = velocity of electron and

$r$  = the distance from the nucleus.

Two electrons having the same direction of spin are said to have parallel spin while the two having opposite spins are said to possess anti-parallel spin.

## Quantum numbers and orbitals

$n$	$l$	Orbital	$m$	No. of orbitals	$s$	No. of electrons in orbitals	Total number of electrons
1	0	1s	0	1	$\pm \frac{1}{2}$	$s^2$ } 2	2
2	0	2s	0	1	$\pm \frac{1}{2}$	$s^2$ } 2 $p^6$ } 6	8
	1	2p	$\pm 1, 0$	3	$\pm \frac{1}{2}$		
3	0	3s	0	1	$\pm \frac{1}{2}$	$s^2$ } 2 $p^6$ } 6 $d^{10}$ } 10	18
	1	3p	$\pm 1, 0$	3	$\pm \frac{1}{2}$		
	2	3d	$\pm 2, \pm 1, 0$	5	$\pm \frac{1}{2}$		
4	0	4s	0	1	$\pm \frac{1}{2}$	$s^2$ } $p^6$ } $d^{10}$ } $f^{14}$ }	32
	1	4p	$\pm 1, 0$	3	$\pm \frac{1}{2}$		
	2	4d	$\pm 2, \pm 1, 0$	5	$\pm \frac{1}{2}$		
	3	4f	$\pm 3, \pm 2, \pm 1, 0$	7	$\pm \frac{1}{2}$		
			and so on.				

$n$	Main shell designation	Values of $l$ 0 to $(n-1)$	Orbital designation ( $nl$ )	Values of $m$ ( $2l+1$ ) 0, $\pm 1$ , $\pm 2$ , $\pm 3$	Designation of orbitals
1	K	0	1s	0	1s
2	L	0	2s	0	2s
		1	2p	+1	2py or 2px
				0	2pz
-1	2px or 2py				
3	M	0	3s	0	3s
		1	3p	+1	3py or 3px
				0	3pz
				-1	3px or 3py
		2	3d	+2	3dxy or $3d_{x^2-y^2}$
				+1	3dxz or 3dyz
				0	$3dz^2$
				-1	3dyz or 3dxz
-2	$3d_{x^2-y^2}$ or 3dxy				

**Example 7.** Write correct orbital notation for each of the following set of quantum numbers :

(i)  $n = 1 \quad l = 0 \quad m = 0$

(ii)  $n = 2 \quad l = 1 \quad m = 1$

(iii)  $n = 3 \quad l = 2 \quad m = -1$

**Solution :** Quantum numbers      Orbital notation

$n = 1, l = 0, m = 0$        $1s$

$n = 2, l = 1, m = 1$        $2p_y$  or  $2p_x$

$n = 3, l = 2, m = -1$        $3d_{xz}$  or  $3d_{yz}$

**Example 8.** What are  $n, l$  and  $m$  values for  $3s, 3p_x$  and  $3d_{xy}$  ?

**Solution :** Orbital notation      Values of

	$n$	$l$	$m$
$3s$	3	0	0
$3p_x$	3	1	-1
$3d_{xy}$	3	2	+2

### • 1.8. NORMALIZED AND ORTHOGONAL WAVE FUNCTIONS

We have discussed the significance of  $\psi$  and  $\psi^2$ . The function  $\psi^2$  is said to be proportional to the probability of the electron in a given volume element,  $dx \, dy \, dz$ . If  $\psi$  is a solution of wave equation, multiplication by a constant 'A' will give wave function, i.e.,  $A\psi$ , which is solution of wave equation. Therefore, we may state that :

$$\int \psi \psi^* \, dx \, dy \, dz \neq \text{Probability}$$

It is proportional to probability. Its square of resultant wave function is probability.

Since the probability of a certainty is defined as unity hence the following relation is established :

$$\int \psi \psi^* \, dx \, dy \, dz = 1$$

If any wave function which satisfies the above relation then it is known as Normalized wave function.

When wave function  $\psi$  is multiply by a constant 'A' we get a new wave function  $A\psi$ . If this new wave function is to be a normalised wave function then

$$\int A\psi \cdot A\psi^* \, dx \, dy \, dz = 1$$

Since A is a constant known as normalized constant hence

$$A^2 \int \psi \cdot \psi^* \, dx \, dy \, dz = 1$$

or 
$$\int \psi \psi^* \, dx \, dy \, dz = \frac{1}{A^2} = A^{-2}$$

Evidently from the above equation, the value of A can be calculated.

Let  $\psi_i$  and  $\psi_j$  be two different acceptable wave functions of a given system. These will be normalized wave function if they satisfy the following equations :

$$\int \psi_i \psi_i^* \, dx \, dy \, dz = 1$$

or 
$$\int \psi_j \psi_j^* \, dx \, dy \, dz = 1$$

On the other hand, if the following relations are satisfied,

$$\int \psi_i \psi_j^* \, dx \, dy \, dz = 0$$

or 
$$\int \psi_j \psi_i^* \, dx \, dy \, dz = 0$$

then these are known as mutually orthogonal wave functions.

**PAULI'S EXCLUSION PRINCIPLE**

In 1925 Pauli put forward a very important principle which controls the assignment of values of four quantum numbers. This principle states that "It is impossible for any two electrons in the same atom to have all the four quantum numbers identical." Thus, in the same atom, any two electrons may have three quantum numbers identical but not the fourth, which must be different.

For example for *K*-shell electrons,

$$\begin{aligned} n=1 \quad l=0 \quad m=0 \quad s=+\frac{1}{2} \\ n=1 \quad l=0 \quad m=0 \quad s=-\frac{1}{2} \end{aligned}$$

This shows that in *K*-shell, there is only one shell  $l=0$  and in this sub-shell only two electrons can be accommodated with spins in opposite direction.

For *L*-shell electrons,

$$\left. \begin{aligned} n=2 \quad l=0 \quad m=0 \quad s=+\frac{1}{2} \\ n=2 \quad l=0 \quad m=0 \quad s=-\frac{1}{2} \end{aligned} \right\} \quad 2 \text{ electrons } (2s^2)$$

$$\left. \begin{aligned} n=2 \quad l=1 \quad m=-1 \quad s=+\frac{1}{2} \\ n=2 \quad l=1 \quad m=-1 \quad s=-\frac{1}{2} \\ n=2 \quad l=1 \quad m=0 \quad s=+\frac{1}{2} \\ n=2 \quad l=1 \quad m=0 \quad s=-\frac{1}{2} \\ n=2 \quad l=1 \quad m=+1 \quad s=+\frac{1}{2} \\ n=2 \quad l=1 \quad m=+1 \quad s=-\frac{1}{2} \end{aligned} \right\} \quad 6 \text{ electrons } (2p^6)$$

Total 8 electrons ( $2s^2 p^6$ )

This shows that in *L*-shell, there are two sub-shells  $l=0$  and  $l=1$ , containing 2 and 6 electrons respectively.

$$\left. \begin{aligned} n=3 \quad l=0 \quad m=0 \quad s=+\frac{1}{2} \\ n=3 \quad l=0 \quad m=0 \quad s=-\frac{1}{2} \end{aligned} \right\} \quad 2 \text{ electrons } (3s^2)$$

$$\left. \begin{aligned} n=3 \quad l=1 \quad m=-1 \quad s=+\frac{1}{2} \\ n=3 \quad l=1 \quad m=-1 \quad s=-\frac{1}{2} \\ n=3 \quad l=1 \quad m=0 \quad s=+\frac{1}{2} \\ n=3 \quad l=1 \quad m=0 \quad s=-\frac{1}{2} \\ n=3 \quad l=1 \quad m=+1 \quad s=+\frac{1}{2} \\ n=3 \quad l=1 \quad m=+1 \quad s=-\frac{1}{2} \end{aligned} \right\} \quad 6 \text{ electrons } (3p^6)$$

$$\left. \begin{aligned} n=3 \quad l=2 \quad m=-2 \quad s=+\frac{1}{2} \\ n=3 \quad l=2 \quad m=-2 \quad s=-\frac{1}{2} \\ n=3 \quad l=2 \quad m=-1 \quad s=+\frac{1}{2} \\ n=3 \quad l=2 \quad m=-1 \quad s=-\frac{1}{2} \\ n=3 \quad l=2 \quad m=0 \quad s=+\frac{1}{2} \\ n=3 \quad l=2 \quad m=0 \quad s=-\frac{1}{2} \end{aligned} \right\} \quad 10 \text{ electrons } (3d^{10})$$

$$\left. \begin{aligned} n=3 \quad l=2 \quad m=+1 \quad s=+\frac{1}{2} \\ n=3 \quad l=2 \quad m=+1 \quad s=-\frac{1}{2} \\ n=3 \quad l=2 \quad m=+2 \quad s=+\frac{1}{2} \\ n=3 \quad l=2 \quad m=+2 \quad s=-\frac{1}{2} \end{aligned} \right\} \quad \text{Total 18 electrons } (3s^2 p^6 d^{10})$$

Evidently according to Pauli's exclusion principle, in *M*-shell (third orbit), maximum number of electrons may be 18. In this there are 2 electrons in  $3s$  subshell ( $3s^2$ ), 6 electrons in  $3p$  subshell ( $3p^6$ ) and 10 electrons in  $3d$  subshell ( $3d^{10}$ ).

Similarly we can explain that *N*-shell (fourth orbit) can accommodate maximum electrons.

### Conclusions of Pauli's Exclusion Principle

1. In any shell ( $n$ ) maximum number of electrons is  $2n^2$ .
2. The number of sub-shells in any shell is equal to the number of shell.
3. The maximum number of electrons in  $s$ -,  $p$ -,  $d$ - and  $f$ - sub-shell is 2, 6, 10 and 14 respectively.
4. The number of orbitals in any shell ( $n$ ) is equal to  $n^2$ .
5. There may be only two electrons of opposite spin in any orbital.

**Example 9.** Write all the values of azimuthal and magnetic quantum number for principal quantum number 2.

**Solution :** For principal quantum number ( $n$ ) 2 the azimuthal quantum number will be 0 and 1. For  $l = 0$ , magnetic quantum number ( $m$ ) = 0 and for  $l = 1$ ,  $m = -1, 0, +1$ .

In other words, for  $n = 2$

$$l = 0, m = 0$$

$$l = 1, m = -1, 0, +1$$

**Example 10.** Write all quantum numbers for  $4s^1$  and  $2p^1$  electrons.

**Solution :** For  $4s^1$  electron :

$$n = 4, l = 0, m = 0 \text{ and } s = +\frac{1}{2}$$

and for  $2p^1$  electron :  $n = 2, l = 1, m = 1 \text{ and } s = +\frac{1}{2}$ .

### • 1.9. HUND'S RULE OF MAXIMUM MULTIPLICITY

On the basis of magnetic measurements, **Hund** postulated an important empirical rule which is generally, known as Hund's rule of maximum multiplicity. This rule may be defined as :

(a) Electrons never pair until no available empty orbitals are left to them. In other words, pairing must begin with the introduction of second electron in the  $s$ -orbital, the fourth electron in the  $p$ -orbitals, the sixth electron in the  $d$ -orbitals and eighth electron in the  $f$ -orbital.

(b) The electrons entering the different orbitals of a sub-shell have parallel spins.

(c) In a given sub-shell ( $n$  and  $l$  values fixed) electrons avoid entering the same orbital as far as possible.

No doubt all the above definitions are identical and carry same meaning that :

"The pairing of electrons will not occur in any orbital until unless all the available orbitals of same energy level have one electron each."

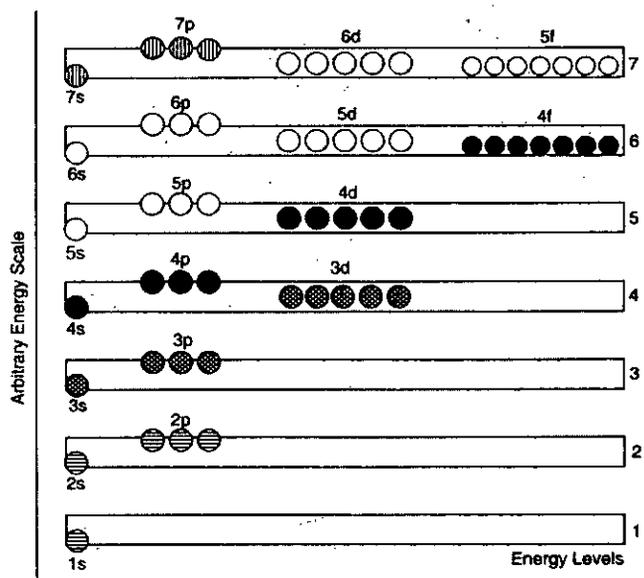
We observe that the electronic configuration of carbon is  $1s^2 2s^2 2p_x^1 2p_y^1$  and not  $1s^2 2s^2 2p_z^2$ . Similarly, in nitrogen, the electronic configuration of  $p$ -orbitals is  $2p_x^1 2p_y^1 2p_z^1$  and not  $2p_x^2 2p_y^1$ . This is in accordance with Hund's rule of maximum multiplicity.

Evidently the pairing of electrons take place from second, fourth, sixth and eighth electron in  $s$ -,  $p$ -,  $d$ - and  $f$ -orbital respectively. In general clockwise spin and anticlockwise spin of the electron as upward arrow ( $\uparrow$ ) and downward arrow ( $\downarrow$ ) respectively. The paired electron in any orbital is shown as ( $\uparrow\downarrow$ ) or ( $\uparrow\downarrow$ ).

### • 1.10. ENERGY LEVELS OF DIFFERENT ORBITALS

It is interesting to note that energy levels of different orbitals calculated by Schrodinger's wave equation for hydrogen and hydrogen like ions (such as  $\text{He}^+$ ,  $\text{Li}^{2+}$ ,  $\text{Be}^{3+}$  etc.) are in close agreement with the values obtained from hydrogen spectra. It means that energy level of all the orbitals in the given principal quantum number is the same.

For example, *the energy level of 3s, 3p and 3d orbitals is the same for hydrogen atom.* But it is not true for multi electron atom. It is seen that in a multi-electron atom,



Energy level diagram of multi-electron atoms.

different orbitals even in the same principal quantum number have different energy levels. This is due to the fact that in such cases energy levels are not only dependent upon the value of  $n$  but also on the values of  $l$ . Therefore  $2s$  and  $2p$  orbitals do not have same energy level and so on. Due to difference in energy level in the same principal quantum number it is possible that a particular orbital of higher principal quantum number may have less energy than the orbital of lower principal quantum number. The energy level of different orbitals is given as :

$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < 6p < 7s < 5f < 6d < 7p$$

The above order of energy level is shown above.

**Aufbau Principle :** Aufbau is a German word meaning 'build up' or *construction*. The principle states that in ground state of atom the electrons reside in the lowest energy sub-shells available to them. In other words sub-shells are filled in order of increasing energy level. According to this rule, a new electron can enter in the sub-shell when  $(n + l)$  is minimum. In case  $(n + l)$  has the same value for two or more sub-shells the electron enters the sub-shell for which  $n$  is minimum. This approximate rule, sometimes called **Madelung's rule**, has some theoretical justification.

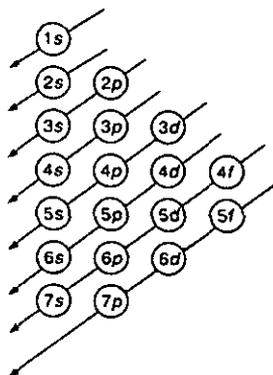
For example,

Sub-shell	$n$	$l$	$(n+l)$
1s	1	0	1
2s	2	0	2
2p	2	1	3
3s	3	0	3
3p	3	1	4
4s	4	0	4
—	—	—	—
—	—	—	—

The usual sequence in which the filling of sub-shells take place is :

1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d, 7p, 8s etc.

The above sequence of energy level can be easily remembered by the diagram shown here.



Sequence of the filling of various sub-shells

**Exception of Aufbau Principle :** There are certain elements *e.g.* Cr, Cu, Ag, Au etc. whose electronic configuration is not according to Aufbau principle. For example,

According to this principle the electronic configuration of chromium (24) should be  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^4 4s^2$  but actually it is  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$ .

Similarly, for copper (29)  ${}_{29}\text{Cu} = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^9 4s^2$  but actually it is  ${}_{29}\text{Cu} = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$

This is due to the fact that half filled and completely filled sub-shells (or orbitals) are more stable.

Element	Electronic configuration according to Aufbau principle	Actual electronic configuration
Cr (24)	$3d^4 4s^2$	$3d^5 4s^1$
Cu (29)	$3d^9 4s^2$	$3d^{10} 4s^1$
Pd (46)	$4d^8 5s^2$	$4d^{10}$
Ag (47)	$4d^9 5s^2$	$4d^{10} 5s^1$
Au (79)	$5d^9 6s^2$	$5d^{10} 6s^1$

**Filling of Electrons in Atomic Orbitals (or sub shells)**

The distribution of electrons in various orbitals is known as electronic configuration of the atom. It proceeds according to the following rules :

(i) The electrons are added one by one to various orbitals as we move from one element to the next in the order of increasing atomic numbers.

(ii) The electronic configuration is represented as  $nl^x$  where  $n$  is principal quantum number, its value may be 1, 2, 3, 4, ... The values of azimuthal quantum number

number 0, 1, 2, 3 are represented as *s*, *p*, *d*, *f* respectively. *x* is the number of electrons present in a particular sub shell. For example electronic configuration of He is  $1s^2$ . It indicates that there are two electrons in first orbit and *s*-sub shell i.e.  $l = 0$ .

(iii) Fill the electrons according to increasing energy level of the sub-shells or obey **Aufbau principle**.

(iv) An orbital cannot contain more than two electrons. This is based on **Pauli's exclusion principle**.

(v) Electrons never pair until no available empty orbitals of same energy are left to them. This is known as **Hund's rule**.

(vi) Energy level tend to become filled or exactly half filled of electrons. This is due to the fact that every system tries to acquire minimum energy for its stability and it is acquired by symmetry of the orbitals. Therefore one electron from the lower energy level goes to higher energy level. For example, the electronic configuration of chromium atom is  $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^5, 4s^1$  and not  $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^4, 4s^2$ . The reason is simple that  $3d^5$  being a half filled sub-shells is more stable than  $3d^4$ . Similarly, the electronic configuration of copper atom is  $[Ar], 3d^{10} 4s^1$  and not  $[Ar], 3d^9, 4s^2$ . Because the  $3d^{10}$  being a completely filled subshells is more stable than  $3d^9$ .

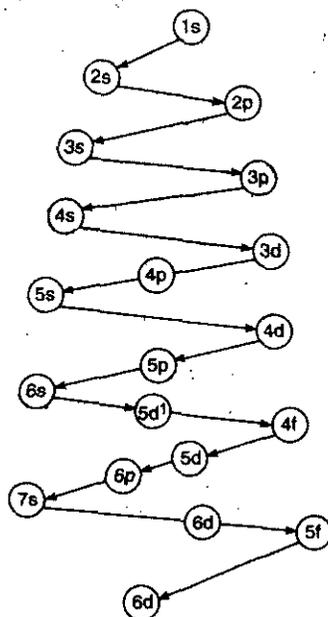
(vii) The electronic configuration of **lanthanides** ( $_{58}\text{Ce}$  to  $_{71}\text{Lu}$ ) and **actinides** ( $_{90}\text{Th}$  to  $_{103}\text{Lw}$ ) is little different from the arrangement for other elements. The electronic configuration of  $_{56}\text{Ba}$  is  $[\text{Xe}] 6s^2$ , the next electron in  $_{57}\text{La}$  enters in  $5d$  subshell and not  $4f$ -subshell i.e. La is  $[\text{Xe}] 5d^1 6s^2$ . However the subsequent electrons in the remaining elements of lanthanides enter the  $4f$ -subshell (but not in  $5d$ -subshell) in accordance to the arrangement as given for the other elements i.e.  $_{58}\text{Ce}$ :  $[\text{Xe}] 4f^1 5d^1 6s^2$ . The filling of  $5d$ -subshell is restarted from  $_{72}\text{Hf}$ :  $[\text{Xe}] 4f^{14} 5d^2 6s^2$  only when the  $4f$ -subshell is completely filled up as in  $_{71}\text{Lw}$ :  $[\text{Xe}] 4f^{14} 5d^1 6s^2$ .

Similarly the electronic configuration of  $_{89}\text{Ac}$  is  $[\text{Rn}] 6d^1 7s^2$ . Now in the case of  $_{90}\text{Th}$  the next electron enters in  $5f$ -subshell (not a  $6d$ -subshell). Therefore the electronic configuration of  $_{90}\text{Th}$  is  $[\text{Rn}] 5f^1 6d^1 7s^2$ . The filling of  $6d$ -subshell is restarted after  $_{103}\text{Lw}$   $[\text{Rn}] 5f^{14} 6d^1 7s^2$ .

The electronic configuration of first thirty elements is given here.

#### Electronic configuration of the elements

Element	Atomic number	K 1s	L 2s 2p	M 3s 3p 3d	N 4s 4p 4d 4f	O 5s 5p 5d 5f	P 6s 6p 6d	Q 7s
H	1	1						
He	2	2						
Li	3	2	1					
Be	4	2	2					
B	5	2	2 1					
C	6	2	2 2					
N	7	2	2 3					
O	8	2	2 4					
F	9	2	2 5					



Alternative sequence of filling

Ne	10	2	2 6					
Na	11	2	2 6	1				
Mg	12	2	2 6	2				
Al	13	2	2 6	2 1				
Si	14	2	2 6	2 2				
P	15	2	2 6	2 3				
S	16	2	2 6	2 4				
Cl	17	2	2 6	2 5				
Ar	18	2	2 6	2 6				
K	19	2	2 6	2 6	1			
Ca	20	2	2 6	2 6	2			
Sc	21	2	2 6	2 6 1	2			
Ti	22	2	2 6	2 6 2	2			
V	23	2	2 6	2 6 3	2			
Cr	24	2	2 6	2 6 5	1			
Mn	25	2	2 6	2 6 5	2			
Fe	26	2	2 6	2 6 6	2			
Co	27	2	2 6	2 6 7	2			
Ni	28	2	2 6	2 6 8	2			
Cu	29	2	2 6	2 6 10	1			
Zn	30	2	2 6	2 6 10	2			

#### • SUMMARY

- Bohr successfully explained the structure of H-atom and hydrogen like ion such as  $\text{He}^+$ ,  $\text{Li}^{++}$ ,  $\text{Be}^{3+}$  etc. But there are certain limitations.
- In hydrogen spectrum five series of lines are observed which are known as Lyman, Balmer, Paschen, Brackett and Pfund series.
- According to de Broglie, the wavelength ( $\lambda$ ) of a particle of mass  $m$  and velocity  $u$  is given by the relation  $\lambda = h / mu$ .
- **Heisenberg's uncertainty principle** : It is impossible to determine simultaneously both the position and velocity (or momentum) of a small moving particle like an electron.
- The **Schrodinger's wave equation** may be given as :
 
$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{h} (E - V) \psi = 0$$
- Schrodinger wave equation can be written in polar coordinates ( $r, \theta, \phi$ ) in place of cartesian coordinates ( $x, y, z$ ). Polar equation is very useful about the study of orbitals.
- The shape of  $s$ ,  $p$ ,  $d$  and  $f$  orbital can be explained by polar coordinate equation.
- The number of nodes in any orbital may be calculated by  $(n - l - 1)$ .
- There are four quantum numbers (Q. No.) such as principal Q. No., Azimuthal Q. No., Magnetic Q. No. and Spin Q. No. which are represented by  $n, l, m$  and  $s$  respectively.
- **Hund's rule** : Electrons are distributed among the orbitals of a sub-shell in such a way as to give the maximum number of unpaired electrons and have the same direction of spin.
- According to **Pauli's exclusion principle**, No two electrons in a given atom can have the same four quantum numbers.
- According to **Aufbau's principle** the electrons are first accommodated in the orbital of lowest energy viz.  $1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d$  etc.

**• STUDENT ACTIVITY**

1. Write the postulates of Bohr's theory of atom.

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2. Discuss the spectrum of hydrogen atom.

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3. Derive de Broglie's equation.

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4. State Heisenberg's uncertainty principle.

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5. Describe Schrodinger wave equation.

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6. Discuss briefly Radial and Angular wave functions.

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7. Describe all the four quantum numbers.

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8. Write a note on Pauli's exclusion principle.

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9. Write a note on Hund's rule.

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10. Discuss  $(n + l)$  rule for distribution of electrons as different orbitals of an atom.

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• TEST YOURSELF

Answer the following questions :

- Describe Bohr's model of hydrogen atom and its limitations.
- Describe the spectrum of hydrogen atom.
- Derive de Broglie's matter wave equation.
- Derive Schrodinger's wave equation.
- Discuss the significance of  $\psi$  and  $\psi^2$ .
- Explain the differences between orbit and orbital.
- Describe quantum numbers.
- Write short note on :
  - Hund's rule
  - Pauli's exclusion principle
  - Heisenberg's uncertainty principle
  - Aufbau principle
- Draw the shapes of *s*, *p* and *d* orbitals.
- How do you distribute the electrons in different orbitals ? Write the electronic configuration of the atoms of atomic numbers 7, 24, 28 and 29.
- What do you mean by node and nodal plan ?
- The kinetic energy of an electron is  $5.76 \times 10^{15}$  J. Find out its wavelength. ( $m_e = 9.1 \times 10^{-31}$  kg,  $h = 6.626 \times 10^{-34}$  Js).
- Calculate the energy emitted by an excited atom which gives a spectral line with values  $n_1$  and  $n_2$  equal to 3 and 5 respectively.
- Find the uncertainty in the position of an electron having uncertainty in the velocity  $6 \times 10^{-4}$  m s<sup>-1</sup>.
- de-Broglie's equation is :
  - $\lambda = \frac{mv}{h}$
  - $\lambda = \frac{h}{mv}$
  - $\lambda = hmv$
  - $\lambda = \frac{1}{hmv}$
- The preference of three unpaired electrons in the nitrogen atom can be explained by
  - Pauli's exclusion principle
  - Hund's rule
  - Aufbau principle
  - None of these
- Magnetic quantum number is related with :
  - Shape of the orbital
  - Size of the orbital
  - Orientation of the orbital
  - Spin of the electron
- p-orbital can accommodate ..... electrons.
  - 2
  - 6
  - 10
  - 14
- Aufbau principle is not correct for :
  - Cr and Ar
  - Cr and Zn
  - Cr and Cu
  - Ar and Zn
- According to Heisenberg's uncertainty principle :
  - $E = mc^2$
  - $\Delta x \times \Delta p = \frac{h}{4\pi}$
  - $\Delta x \times \Delta v = \frac{h}{4\pi}$
  - $\Delta x \times \Delta p = \frac{h}{\pi}$
- Which one of the following orbitals is symmetrical about x-axis :
  - $p_x$
  - $p_y$
  - $p_z$
  - $d_{z^2}$
- If  $l = 3$ , then the values of magnetic quantum number will be :
  - 0
  - $\pm 3, \pm 2, \pm 1, 0$
  - $\pm 2, \pm 1, 0$
  - All the above
- Which one of the following electronic configurations is not possible :
  - $1s^2 2s^2 2p^5$
  - $1s^2 2s^2 2p^6$
  - $1s^2 2s^2 2p^7$
  - $1s^2 2s^2$
- Fill in the blanks :
  - The number of unpaired of the atom of atomic number 7 are .....

- (ii) If there are two electrons in an orbital, their spin is .....
- (iii) The electronic configuration of the atom of atomic number 24 is .....
- (iv) The sphere of  $p$ -orbitals is .....
25. Identify True (T) and False (F) statements.
- (i) The de-Broglie's equation may be applied for atomic particles.
- (ii) The energy level of  $3d$ -orbital is more than that of  $4s$ -orbital.
- (iii) The electron density in the  $xy$  plane of  $3d_{x^2-y^2}$  orbital is maximum.
- (iv) There are three nodal plane for  $3s$ -orbital.

### ANSWERS

12.  $0.065\text{\AA}$       13.  $1.55 \times 10^{-22} \text{ kJ}$       14.  $0.1926 \text{ m}$       15. (b)      16. (b)
17. (c)      18. (a)      19. (c)      20. (b)      21. (a)
22. (b)      23. (c)      24. (i) Three, (ii) Opposite,
- (iii)  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$  (iv) dumbell shape 25. (i) T, (ii) T, (iii) F, (iv) F.

# UNIT

## 2

### CHEMICAL BONDING

#### STRUCTURE

- Ionic or Electrovalent Bond
- General Characteristics
- Types of Ions and Radius Ratio Rule
- Packing of Ions
- Born-Landé's Equation and Madelung Constant
- Born-Haber Cycle and Solvation Energy
- Covalent Bond
- Valence Bond Theory (VBT)
- Hybridisation
- Bent's Rule and Resonance
- Molecular Orbital Theory (MOT)
- Formal Charge
- Valence Shell Electron Pair Repulsion (VSEPR) Theory
- Shape of the Molecules
- Bond Length
- Fajan's Rule
- Dipole Moment and Ionic Character
- Summary
- Student Activity
- Test Yourself
- Answers

#### LEARNING OBJECTIVES

After going this unit you will learn :

- Nature of the ionic bond and types of the ions
- Packing of ions in the ionic crystal
- Thermal stability of the ionic compounds
- $sp^3$ ,  $sp^2$  and  $sp$  hybridization and shapes of covalent molecules
- VBT and MOT for covalent compounds
- Shapes of the molecules possessing lone pair/s of electrons
- Polarity of the molecules

#### • 2.1. IONIC OR ELECTROVALENT BOND

According to electronic theory of valency, every element has a tendency to occupy inert gas configuration ( $ns^2 np^6$ ) of the nearest gas. This configuration may be attained by transference of electron(s) (Ionic valency) or by sharing of electron(s) (Covalency) or by donation of lone pair(s) of electrons (Coordinate valency).

Thus ionic or electrovalent bond is formed by the transference of one or more electrons from one atom to another. It depends upon following three major factors.

- (i) Electron affinity of one atom should be high.
- (ii) Ionisation energy of second atom should be low.

(iii) Lattice energy of the compound formed should be high.

Accordingly the properties of the ionic compounds varies.

## • 2.2. CHARACTERISTICS OF ELECTROVALENT COMPOUNDS

(i) They are hard crystalline solids. Hardness of these compounds increases with decrease in the inter-ionic distances and increase in the ionic charge.

(ii) These compounds have high melting and boiling points. Because there is a powerful electrostatic force of attraction between the ions in the crystal lattice.

(iii) They are soluble in polar solvents like water and liquid ammonia, but insoluble in organic solvents. Some compounds such as sulphate and phosphate of barium are insoluble in water. This is due to the fact that their lattice energy is higher than solvation energy.

(iv) They have polar nature. The linkage between the oppositely charged ions (poles) is non rigid and non directional.

(v) In crystalline state they are bad conductor of electricity because ions are not movable. But their aqueous solutions conduct electricity due to availability of free ions.

(vi) They are incapable of exhibiting any type of isomerism.

(vii) They undergo fast reactions.

(viii) They are highly brittle.

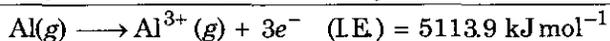
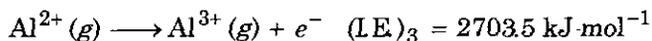
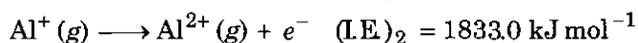
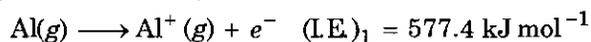
(ix) They have high density.

## • 2.3. TYPES OF IONS

Ions are of two types, known as *cations* and *anions*.

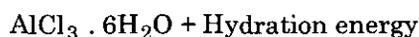
### Formation of Cations

These are formed by the removal of electron(s) from the outermost orbit of the atom. As the number of removal electron increases, charge on the cation increases and it becomes more and more difficult. In other words, it is easier to form univalent cation than divalent cation and trivalent cation etc. To explain this we consider the formation of  $\text{AlCl}_3$  (s). It is a covalent compound, but in aqueous solution it becomes ionic compound or it forms  $\text{Al}^{3+}$  (aq). The reason is that the sum of first three ionisation energies is very large ( $5113.9 \text{ kJ mol}^{-1}$ ).



while rarely more than  $1500 \text{ kJ mole}^{-1}$  energy is available when combination of atoms takes place. Due to this fact, generally the elements of 13 and 14 groups do not form ionic compound.

But when  $\text{AlCl}_3$  (s) is added in water it liberates too much energy (i.e., hydration energy is very large). This available energy is sufficient to release three electrons from aluminium atom and it becomes trivalent aluminium ion ( $\text{Al}^{3+}$ ).



It is clear from the discussion that why does Al not form  $\text{Al}^{3+}$  ion easily and it forms covalent compounds preferably. In the same way we can discuss other examples of the elements of group 14.

### Formation of Anions

Anions are formed by the addition of electron(s) to the neutral atom which is related to electron affinity. The elements of groups 17 and 16 form anions of one and two negative charge easily, this has been discussed. Now we consider the formation of  $N^{3-}$  and  $P^{3-}$  ions (group 15). To get these ions three electrons are to be added in nitrogen atom which requires too much energy, which is ordinarily not available in chemical reactions. Hence the formation of such ions is rare. In the same way we may explain for other atoms of group 15. In the case of the elements of group 14 it is too difficult to form  $C^{4-}$ ,  $Si^{4-}$  ions etc.

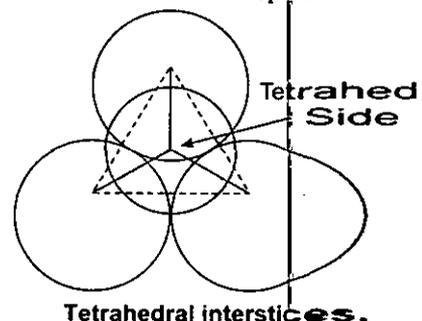
**Size Effect :** The size of the cation is always smaller than that of the corresponding atoms. It is due to increase of effective nuclear charge ( $Z_{eff}$ ). As the charge on the cation increases,  $Z_{eff}$  increases and size of the cation decreases i.e., order of size of the cation is  $M > M^+ > M^{2+} > M^{3+}$  and so on. On the other hand the size of the anion is always greater than that of the corresponding atoms. It is due to the decrease of the  $Z_{eff}$ . As the charge on the anion increases,  $Z_{eff}$  decreases and size of the anion increases i.e., order of size of the anion is  $M < M^- < M^{2-}$  and so on.

### Packing of Ions in Crystals

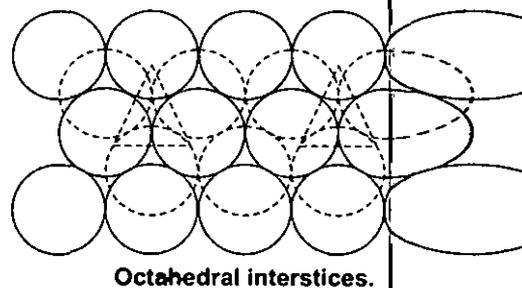
In ionic crystals the units occupying lattice points are cations and anions. These are closely packed. For example in NaCl, the units are  $Na^+$  ions and  $Cl^-$  ions. Oppositely charged ions are held by coulombic force of attraction which are very strong. Therefore the amount of energy required to separate ions from one another is very high.

It has been shown that the particles are closely packed in the crystals even though there is some empty space left in between the spheres. This is known as interstices (or interstitial site or holes or empty space or voids). The interstices are of two types :

(i) **Tetrahedral interstices :** We have seen that in hexagonal close packing (hcp) and cubic close packing (ccp) each sphere of second layer touches with three spheres of first layer. Thus they leave a small space in between which is known as tetrahedral site or interstices (figure). Since a sphere touches three spheres in the below layer and three spheres of the above layer hence there are two tetrahedral sites associated with one sphere. *It may be noted that a tetrahedral site does not mean that the site is tetrahedral in geometry but it means that this site is surrounded by four spheres and the centres of these four spheres lie at the apices of a regular tetrahedron.*



(ii) **Octahedral interstices :** Hexagonal close packing (hcp) and cubic close packing (ccp) also form another type of interstices (or sites) which is called octahedral site (or interstices). In figure two layers of close packed spheres are shown. The spheres of first layer are shown by full circles while those of second layer by dotted circles. Two triangles are drawn by joining the centres of three touching spheres of both the layers. The apices of these triangles point are in opposite directions. On super-imposing these triangles on one another an octahedral site is created. *It may be noted that an octahedral site does not mean that the hole is octahedral in shape but it means that this site is surrounded by six nearest neighbour lattice points arranged octahedrally.*



## • 2.4. RADIUS RATIO RULE

We know that, in ionic crystals, the coordination number of ions and geometric shapes of the crystal depends upon their radius ratio ( $r/R$ ).

Let us discuss the role of radius ratio by taking the example of molecule  $AB_3$ . Therefore  $A^+$  is surrounded by three  $B^-$  ions. If the size of  $A^+$  is such that all the three  $B^-$  ions are touching with each other as well as with  $A^+$  ( $r/R \approx 0.155$ ). In this case force of attraction among oppositely charged ions is quite strong. But the  $B^-$  ions are also touching with each other therefore there will be stronger repulsion. If the size of  $A^+$  is bigger (i.e.,  $r/R > 0.155$ ), the force of attraction will be quite strong but force of repulsion due to  $B^-$  ions will be quite small. If the size of  $A^+$  is smaller (i.e.,  $r/R < 0.155$ ) i.e.,  $A^+$  ion is not touching  $B^-$  ions the force of attraction will be weak and force of repulsion will be high i.e. crystal will be unstable.

In short we may state that radius ratio ( $r/R$ ) ranging between 0.155–0.225 trigonal site will be preferred in which coordination number of cation is 3.

Similarly  $r/R$  ranging between 0.225–0.414 tetrahedral site will be preferred in which coordination number of cation is 4. In the range 0.414–0.732, octahedral site (C.N. of cation 6) will be adopted by the cation. Above 0.732 cubic site (C.N. of cation 8) will be favoured.

Evidently radius ratio ( $r/R$ ) plays a very important role in deciding the stable structure of ionic crystal. Larger cations prefer occupying larger holes (cubic etc.) and smaller cations prefer occupying smaller holes (tetrahedral etc.). The preferred direction of the structure with increase in the radius ratio is as follows :

Plane triangular  $\xrightarrow{0.225}$  Tetrahedral  $\xrightarrow{0.414}$  Octahedral  $\xrightarrow{0.732}$  Cubic

Limiting Radius Ratio for Various Types of Sites

$r/R$	Coordination number of cation	Structural arrangement	Example
0.155 – 0.225	3	Plane Trigonal	Boron oxide
0.225 – 0.414	4	Tetrahedral	ZnS
0.414 – 0.732	4	Square Planar	—
0.414 – 0.732	6	Octahedral	Sodium halides, AgCl, MgO
0.732 – 1.000	8	Cubic	CsCl, CsBr, TlCl

**Example 1.** A solid  $A^+ B^-$  has NaCl type close packed structure. If the anion has a radius of 250 pm what should be the ideal radius for the cation? Can a cation  $C^+$  having a radius of 180 pm be slipped into the tetrahedral site of the crystal  $A^+ B^-$ ? Give reason for your answer.

**Solution.** In  $Na^+ Cl^-$  crystal each  $Na^+$  ion is surrounded by 6  $Cl^-$  ions and vice versa. Thus  $Na^+$  ion is placed in octahedral hole.

The limiting radius ratio of octahedral site = 0.414

or 
$$\frac{r}{R} = 0.414$$

Given that  $R = 250$  pm

$$\therefore r = 0.414R = 0.414 \times 250 \text{ pm} \quad \text{or} \quad r = 103.5 \text{ pm}$$

Thus, ideal radius for cation ( $A^+$ ) is 103.5 pm.

We know that ( $r/R$ ) for tetrahedral hole is 0.225.

$$\therefore \frac{r}{R} = 0.225$$

or 
$$r = 0.225R = 0.225 \times 250 = 56.25 \text{ pm}$$

Thus, ideal radius for cation is 56.25 pm for tetrahedral hole. But the radius of  $C^{+}$  is 180 pm. It is much larger than ideal radius i.e., 56.25 pm. Therefore we cannot slip cation  $C^{+}$  into the tetrahedral site.

Summary of Various Structure of Ionic Crystalline Solids

Crystal Structure	Characteristics	$r/R$	Coordination Number	No. of units (AB) per unit cell	Examples
1. Rock salt (NaCl-type)	$Cl^{-}$ ions in ccp, $Na^{+}$ ions occupy all octahedral voids.	0.414–0.732	$Na^{+} \rightarrow 6$ $Cl^{-} \rightarrow 6$	4	Halides of Li, Na, K and Rb $NH_4Cl$ , $NH_4Br$ , $NH_4I$ , $AgF$ , $AgBr$ , Oxides of Mg, Ca, Ti, Fe, Ni
2. Zinc blende (ZnS-type)	$S^{2-}$ ions in ccp, $Zn^{2+}$ ions occupy alternate tetrahedral voids.	0.225 – 0.414	$Zn^{2+} \rightarrow 4$ $S^{2-} \rightarrow 6$	4	ZnS, BeS, HgS, CuCl, CuBr, CuI, AgI
3. Wurtzite (ZnS-type)	$S^{2-}$ ions in hcp, $Zn^{2+}$ as in Zinc blends.	0.225 – 0.414	$Zn^{2+} \rightarrow 4$ $S^{2-} \rightarrow 4$	4	ZnS, BeO, CdS, ZnO
4. Caesium Chloride (CsCl-type)	$Cl^{-}$ ions in bcc, $Cs^{+}$ ions in the body of cube.	0.732 – 1.000	$Cs^{+} \rightarrow 8$ $Cl^{-} \rightarrow 8$	1	CsCl, CsBr, CsI, $CsCN$ , CaS
5. Fluorite ( $CaF_2$ -type)	$Ca^{2+}$ ions in ccp, $F^{-}$ ions occupy all tetrahedral voids.	0.225 – 0.414	$Ca^{2+} \rightarrow 8$ $F^{-} \rightarrow 8$	4	Fluorides of Ca, Sr, Ba, Cd, Hg, Chlorides of Ba, Sr
6. Anti-fluorite ( $Li_2O$ -type)	$O^{2-}$ ions in ccp, $Li^{+}$ ions occupy all tetrahedral voids.	0.225 – 0.414	$Li^{+} \rightarrow 4$ $O^{2-} \rightarrow 8$	4	$Na_2O$ , $K_2O$ , $Na_2S$ , $K_2S$

Limitations

Radius ratio rule is applicable only the packing of rigid spheres. But larger anions are easily polarised thus they do not behave as rigid spheres. Due to polarisation, such anions tend to form covalent bonds. Since covalent bonds are directional hence radius ratio rule is not applicable.

It is important to note that although radius ratio value is useful guide to guess the geometry of the molecule, but there are many exceptions where they predict the wrong structure. Therefore it is necessary to examine the assumptions behind the radius ratio concept if they are valid. These assumptions are :

- (i) That bonding is 100% ionic.
- (ii) That ions are spherical in shape.
- (iii) That accurate values of ionic radii are known.
- (iv) That ions behave as hard inelastic spheres.
- (v) That ions always adopt the highest possible coordination number.
- (vi) That stable arrangements are only possible if the cations and anions touch each other.

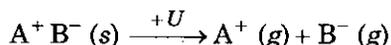
## • 2.5. LATTICE ENERGY IN IONIC SOLIDS

The lattice energy may be defined as, "The amount of energy released when cations and anions (in gaseous state) are brought from infinity to their respective lattice sites in a crystal to form one mole of the ionic solid". It is expressed as  $U$ . Thus,



Since energy is released in this process hence it is an exothermic process. In this process potential energy of the systems decreases. It is important to note according to first law of thermodynamic it should be expressed with negative sign.

On the other hand, if one mole of  $A^+ B^- (s)$  absorbs energy  $U$  to change into  $A^+ (g)$  and  $B^- (g)$  then it will be endothermic process and it has positive sign.



It means higher the value of  $U$ , higher is the stability of the ionic compound.

Evidently the lattice energies of the ionic compounds are very high. This is due to strong force of attraction. The lattice energy decreases as bond length increases and increases as we move from uni-univalent ionic solids, to uni-bivalent ionic solids and to bi-bivalent ionic solids.

### Calculations of Lattice Energy

The lattice energy of ionic solids can be calculated by considering two types of forces operating between the ions of the crystals. These forces are:

(i) Electrostatic forces of attraction acting between oppositely charged ions (cations and anions).

(ii) Repulsive forces due to inter-penetration of electron charge clouds.

Let us calculate the magnitude of these forces considering the example of NaCl.

**(i) Attractive forces between cations and anions :** According to Coulomb's law of inverse square,

$$F = \frac{(Z_1 e)(-Z_2 e)}{r^2}$$

where  $Z_1$  and  $Z_2$  are the charges on the cation and anion,  $e$  is the electronic charge and  $r$  is the bond length (or internuclear distance between the ions).

Now if one of the ions is moved under the influence of attraction of the other from infinity through a small distance  $dr$ , the work done in the process may be given as,

$$\text{Work done} = \frac{(Z_1 e)(-Z_2 e)}{r^2} dr \quad \dots (i)$$

$$\text{On integration Work done} = \int_{r=\infty}^{r=r} \frac{(Z_1 e)(-Z_2 e)}{r^2} dr$$

$$\text{Work done} = \frac{(Z_1 e)(-Z_2 e)}{r}$$

But according to definition, work done is equal to the electrostatic potential energy between the two ions. Thus

$$\text{Attractive potential energy} = \frac{(Z_1 e)(-Z_2 e)}{r} \quad \dots (ii)$$

**(ii) Repulsive interactions due to interpenetration of electron charge clouds :** When cation and anion approach close to each other, there is repulsion between them due to same charge on the electrons. This repulsive interaction may be given as :

$$\text{P.E}_{\text{repulsion}} = \frac{be^2}{r^n} \quad \dots (iii)$$

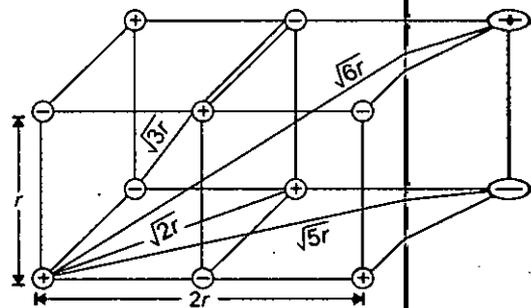
where  $b$  is repulsion coefficient,  $e$  is the electronic charge and  $n$  is called Born exponent. The repulsion coefficient measures the strength of the repulsive force and depends upon the particular ion present. The value of  $n$  depends upon the type of electronic configuration of the ion. Its value increases with increase in electron density around the ions. The value of  $n$  is 7, 9, 10 and 12 for the ion having 10, 18, 36 and 54 electrons respectively.

$$P.E_{\text{net}} = P.E_{\text{attractive}} + P.E_{\text{repulsive}}$$

$$P.E_{\text{net}} = -\frac{Z_1 Z_2 e^2}{r} + \frac{be^2}{r^n} \quad \dots \text{(iv)}$$

The eq. (iv) is called **Born equation**.

It is clear from the eq. (iv) that repulsive forces increase more rapidly than attractive forces as the value of  $r$  decreases. Born equation is mainly used in the calculation of energy released if a cation and anion, which are separated by an infinite distance in gaseous state are brought together in a crystal at a distance  $r$  from each other.



Inter-ionic distance in NaCl crystal.

Now, we illustrate the application of Born equation to a NaCl crystal. We know that in NaCl crystal  $\text{Na}^+$  and  $\text{Cl}^-$  ions are arranged in a definite geometry. Therefore it is necessary to consider  $P.E_{\text{attractive}}$  and  $P.E_{\text{repulsive}}$  between all of them.

In a crystal of NaCl (figure) the potential at a  $\text{Na}^+$  results from

- (i) 6  $\text{Cl}^-$  ions at a distance  $r$ .
- (ii) 12 other  $\text{Na}^+$  ions at a distance  $\sqrt{2}r$
- (iii) 8 more  $\text{Cl}^-$  ions at a distance  $\sqrt{3}r$
- (iv) 6 other  $\text{Na}^+$  ions at a distance  $2r$ .
- (v) 24 more  $\text{Cl}^-$  ions at a distance  $\sqrt{5}r$ .
- (vi) 24 more  $\text{Na}^+$  ions at a distance  $\sqrt{6}r$  and so on.

Using the above data, potential energy may be calculated as :

$$(P.E)_1 = -\frac{6e^2}{r} + \frac{12e^2}{\sqrt{2}r} - \frac{8e^2}{\sqrt{3}r} + \frac{6e^2}{2r} - \frac{24e^2}{\sqrt{5}r} + \frac{24e^2}{\sqrt{6}r} + \dots$$

$$= -\frac{e^2}{r} \left[ 6 - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{2} + \frac{24}{\sqrt{5}} - \frac{24}{\sqrt{6}} \dots \right] \quad \dots \text{(v)}$$

where  $(P.E)_1$  is the potential energy due to attraction. For  $\text{Na}^+ \text{Cl}^-$  crystal the value of  $Z_1$  and  $Z_2$  is 1. The quantity in the bracket is the sum of an infinite series and is called **Madelung constant** for NaCl crystal. Its value is 1.747558 for NaCl. Since this value depends only on the geometry of the crystal hence all the crystals of NaCl type have the same value of Madelung constant. If this constant is represented by  $A$  then the first term may be expressed as :

$$(P.E)_1 = -\frac{A.Z_1 Z_2 e^2}{r} \quad \dots \text{(vi)}$$

The value of Madelung constants for same common crystal structure are given in the following table :

Madelung constant for some common crystal structure

Crystal Structure	Example	Coordination number of ions	Madelung Constant
Sodium Chloride	NaCl	Na <sup>+</sup> : 6; Cl <sup>-</sup> : 6	1.7475
Cesium Chloride	CsCl	Cs <sup>+</sup> : 8; Cl <sup>-</sup> : 8	1.7627
Zinc blende	ZnS	Zn <sup>2+</sup> : 4; S <sup>=</sup> : 4	1.6381
Wurtzite	ZnS	Zn <sup>2+</sup> : 4; S <sup>=</sup> : 4	1.6410
Fluorite	CaF <sub>2</sub>	Ca <sup>2+</sup> : 8; F <sup>-</sup> : 4	5.0388
Rutile	TiO <sub>2</sub>	Ti <sup>4+</sup> : 6; O <sup>=</sup> : 3	4.8160
Cadmium iodide	CdI <sub>2</sub>	Cd <sup>2+</sup> : 6; I <sup>-</sup> : 3	4.7100

Now we consider the second term of **Born equation**. In NaCl crystal each Na<sup>+</sup> ion is surrounded by 6 Cl<sup>-</sup> ions hence the term  $6be^2/r^n$  may be written as  $6be^2/r^n$  or  $B/r^n$  where  $B = 6be^2$  and is known as, **Born coefficient or repulsion coefficient**. Therefore the equation (iv) may be written as

$$(P.E.)_{\text{net}} = -\frac{A.Z^2 e^2}{r} + \frac{B}{r^n}$$

or 
$$P.E._{\text{net}} = -A.Z^2 e^2.r^{-1} + Br^{-n} \quad \dots \text{(vii)}$$

where  $A = \text{Madelung constant}$ ;  $Z_1$  and  $Z_2$  are replaced by  $Z$  as  $Z_1 = Z_2 = Z$ .

When attractive and repulsive forces are equally balanced a state of stable equilibrium position is attained. Thus the term  $B$  may be eliminated. At this state the potential energy of the ion is minimum and  $d(P.E.)/dr = 0$ . The inter-ionic distance,  $r$  may be taken as  $r_0$ . By differentiating the eq. (vii) with respect to  $r$ , we get

$$\frac{d}{dr}(P.E.) = -\frac{d}{dr}AZ^2e^2r^{-1} + \frac{d}{dr}Br^{-n}$$

or 
$$\frac{d}{dr}(P.E.) = +AZ^2e^2r^{-2} - nBr^{-n-1}$$

When  $r = r_0$ , then  $\frac{d}{dr}(P.E.) = 0$ .

$$0 = +AZ^2e^2r_0^{-2} - nBr_0^{(-n-1)}$$

or 
$$AZ^2e^2r_0^{-2} = nBr_0^{(-n-1)}$$

or 
$$r_0^{n-1} = \frac{nB}{AZ^2e^2}$$

or 
$$r_0 = \left( \frac{nB}{AZ^2e^2} \right)^{\frac{1}{n-1}} \quad \dots \text{(viii)}$$

and 
$$B = \frac{AZ^2e^2r_0^{n-1}}{n} \quad \dots \text{(ix)}$$

On substituting the value of  $B$  in eq. (vii), we get

$$(P.E.)_0 = -\frac{A.Z^2 e^2}{r_0} + \frac{AZ^2 e^2 r_0^{n-1}}{nr_0^n}$$

$$= -\frac{AZ^2 e^2}{r_0} + \frac{AZ^2 e^2}{nr_0}$$

$$= \frac{AZ^2 e^2}{r_0} \left( \frac{1}{n} - 1 \right)$$

Since the unit of lattice energy ( $U_0$ ) is given in per mole hence;

$$U_0 = N_0 \times (\text{P.E.})$$

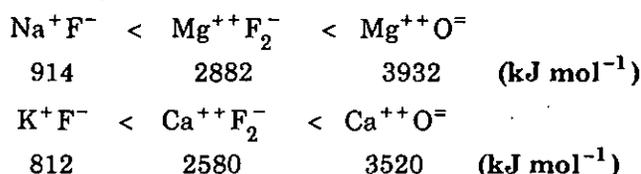
Where  $N_0$  is Avogadro's number

$$\therefore U_0 = \frac{N_0 AZ^2 e^2}{r_0} \left( \frac{1}{n} - 1 \right)$$

Since  $n$  is always more than 1, hence  $U_0$  would be negative. The eq. (xi) is known as **Born-Lande's equation**.

**Conclusions from Born equation :** From eq. (xi) we may derive some important conclusions which are as follows :

(1) The higher the charge on cation and anion, the greater would be the value of lattice energy ( $U_0$ ) or greater would be the stability of the crystal *e.g.*,



(2) The smaller the interionic distance the greater would be the magnitude of lattice energy ( $U_0$ ) or greater would be the stability of the crystal *e.g.*,

Size of $\text{M}^+$ ion	$\text{Li}^+$	$<$	$\text{Na}^+$	$<$	$\text{K}^+$	$<$	$\text{Rb}^+$	$<$	$\text{Cs}^+$
Lattice energy of fluorides (kJ mol <sup>-1</sup> )	1034		914		812		780		744
Size of $\text{X}^-$ ion	$\text{F}^-$	$<$	$\text{Cl}^-$	$<$	$\text{Br}^-$	$<$	$\text{I}^-$		
Lattice energy of $\text{Li}^+$ (kJ mol <sup>-1</sup> )	1034		840		781		718		
Size of $\text{M}^{++}$ ion	$\text{Be}^{++}$	$<$	$\text{Mg}^{++}$	$<$	$\text{Ca}^{++}$	$<$	$\text{Sr}^{++}$	$<$	$\text{Ba}^{++}$
Lattice energy of oxides (kJ mol <sup>-1</sup> )	4540		3932		3520		3325		3108

(3) The higher the value of  $A$  (Madelung constant, which depends upon the coordination number and geometry of the crystal) the greater would be  $U_0$ .

(4) The higher value of  $n$  (Born exponent, which is measurement of the compressibilities of ionic crystal) greater would be the value of lattice energy.

**Kapustinskii** noticed following facts about the ionic crystals :

(i) If the Madelung constants for a number of structures are divided by the number of ions per formula unit, almost same value is obtained for all structures.

(ii) This value increases with increase in coordination number, due to increase of ionic radii with increase in coordination number.

Thus he proposed following equation to calculate the value of lattice energy, known as **Kapustinskii equation**.

$$U_c = \frac{125200 \nu Z_+ Z_-}{r_0} \left[ 1 - \frac{34.5}{r_0} \right]$$

where  $\nu$  is the number of ions per molecule *e.g.*,  $\nu = 3$  for  $\text{BaCl}_2$ ,  $\text{Li}_2\text{O}$  etc. and  $r_0$  is the sum of the ionic radii of the ions.

**Correction of Born-Landé's equation:** The eq. (xi) may be further improved by considering the following correction factors:

- (i) van der Waals forces between the ions.
- (ii) Zero point energy of the crystals. This type of energy is due to vibration of the ion in the crystal.
- (iii) Resonance energy. This type of energy is due to the covalent nature of the ionic bond upto some extent.

**Example 2.** Calculate the lattice energy of NaCl crystal with the help of Born-Landé's equation from the following data:

$$e = 4.8 \times 10^{-10} \text{ e.s.u.}, A = 1.7476, r_0 = 2.76 \text{ \AA}$$

**Solution.** According to Born-Landé's equation,

$$U = \frac{N_0 AZ^2 e^2}{r_0} \left( \frac{1}{n} - 1 \right)$$

Here  $N_0 = 6.023 \times 10^{23} \text{ mol}^{-1}$ ,  $A = 1.7476$ ,  $Z = 1$ ,  $e = 4.8 \times 10^{-10} \text{ e.s.u.}$ ,

$$r_0 = 2.76 \text{ \AA} = 2.76 \times 10^{-8} \text{ cm}, \text{ and } n = (1/2)(7 + 9) = 8$$

[We know that  $n = 7$  for  $\text{Na}^+$  ion and  $n = 9$  for  $\text{Cl}^-$  ion, hence  $n = (7 + 9)/2 = 8$ ].

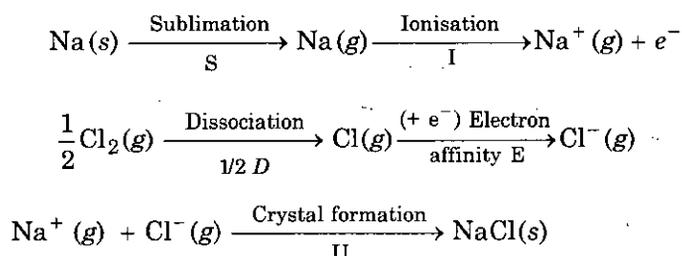
On substituting these values in the above equation

$$\begin{aligned} U &= \frac{6.023 \times 10^{23} \text{ mol}^{-1} (1.7476) (1)^2 (4.8 \times 10^{-10} \text{ esu})^2}{2.76 \times 10^{-8} \text{ cm}} \left( \frac{1}{8} - 1 \right) \\ &= -7.688 \times 10^{12} \frac{(\text{e.s.u.})^2}{\text{cm}} \text{ mol}^{-1} \\ &= -7.688 \times 10^{12} \text{ erg mol}^{-1} \\ &= -7.688 \times 10^5 \text{ J mol}^{-1} \\ &= -768.8 \text{ kJ mol}^{-1} \end{aligned}$$

## • 2.6. BORN-HABER CYCLE :

Since the direct determination of the lattice energy of the compound is not easy hence it is determined indirectly with the help of a thermochemical cyclic process. This cyclic process is known as **Born-Haber cycle**.

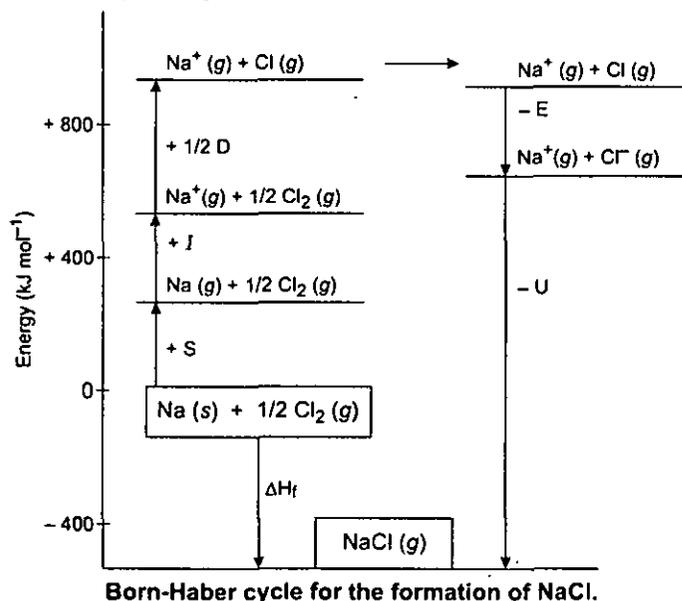
The formation of an ionic compound from its constituent elements proceed in a number of steps. For example, the formation of one mole of sodium chloride from sodium and chlorine atoms may be represented as follows:



where

- $I$  = Ionisation energy of sodium
- $S$  = Sublimation energy of sodium metal
- $D$  = Dissociation energy of molecular chlorine
- $E$  = Electron affinity of chlorine atom
- $U$  = Lattice energy of sodium chloride

The Born-Haber cycle may be represented as :



The enthalpy of formation of sodium chloride ( $\Delta H_f$ ) may be given as :

$$\Delta H_f = S + \frac{1}{2}D + I + E + U$$

The higher is the negative value of heat of formation, the greater will be the stability of ionic compound produced.

**Applications :**

The lattice energy is very important to explain some properties of the ionic crystals.

**(i) Solubility of ionic crystals in different solvents :** When any ionic crystal is dissolved in solvent the crystal lattice is ruptured and crystal dissolves in solvent. The required energy is obtained due to interaction of ions and solvent i.e., solvation of ions. (In the case of water as solvent, then it is called hydration of ion and energy is called hydration energy). If solvation process is an exothermic process then the solvation energy is utilized in rupturing the crystal lattice. Therefore the solvents which have high dielectric constants, such as water, liq.  $\text{NH}_3$ , liq. HF etc., are good solvents for ionic solids. On the other hand the solvents which have low dielectric constants, such as benzene, ether, carbon tetrachloride etc. are not good solvents for ionic compounds.

On the basis of above discussion we can explain the less solubility of the salts of alkaline earth metals (Mg, Ca, Sr, Ba) with polyvalent anions ( $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ ,  $\text{C}_2\text{O}_4^{2-}$  etc.). The lattice energy of such compounds is too higher than their hydration energy.

**(ii) Stability of ionic compounds :** We know that stability of the ionic compound depends upon the lattice energy. The higher value of lattice energy means larger attractive forces between the cations and anions and higher is the stability. Therefore the magnitude properties such as melting point, boiling point, enthalpy of formation and enthalpy of sublimation would be high due to higher lattice energy.

**Example 3.** Calculate the lattice energy of NaCl crystal. The heat of sublimation of sodium is  $108.8 \text{ kJ mol}^{-1}$ , the heat of dissociation of chlorine gas is  $242.7 \text{ kJ mol}^{-1}$ , the ionisation energy of sodium is  $498.3 \text{ kJ mol}^{-1}$ , the electron affinity of chlorine is  $-380.7 \text{ kJ mol}^{-1}$  and the heat of formation of solid sodium chloride from its elements is  $-410.9 \text{ kJ mol}^{-1}$ .

**Solution.** The cycle for the formation of solid sodium chloride can be represented as above.

$$\text{Hence, } \Delta H_f = S + \frac{1}{2}D + I + E + U$$

$$\text{or } -U = S + \frac{1}{2}D + I + E - \Delta H_f$$

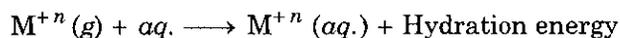
Substituting the different values on the right hand side, we get :

$$-U = 108.8 + \frac{1}{2}(242.7) + 498.3 - 380.7 + 410.9$$

$$\text{or } U = -758.65 \text{ kJ mol}^{-1}.$$

## • 2.7. SOLVATION ENERGY

When an ionic solid is added in solvent, the cations and anions present in ionic solid are surrounded by negative and positive ends of the solvent molecules respectively. As a result of that the charge on cations and anions is partly neutralised and the solvent molecules act as an insulating sphere. This insulating effect is known as dielectric effect. Thus ion-dipole interaction takes place due to which there is loose combination between the ions and solvent molecules is called **solvation** and the energy released in the process is called **solvation energy**. If solvent is water, these terms are called **hydration** and **hydration energy**. For example



Evidently as the hydration energy increases solubility of ionic solid increases. The ions with small size and high charge are heavily hydrated and are having maximum hydration energy. Therefore the order of hydration energy of  $Li^+$ ,  $Na^+$  and  $K^+$  is  $Li^+ > Na^+ > K^+$ .

On the basis of above discussion we may conclude that dissolution of ionic solids in water depends upon their lattice energy and hydration energy. These two terms are related with enthalpy of solution ( $\Delta H$ ) as :

$$\Delta H = \text{Hydration energy} - \text{Lattice energy}$$

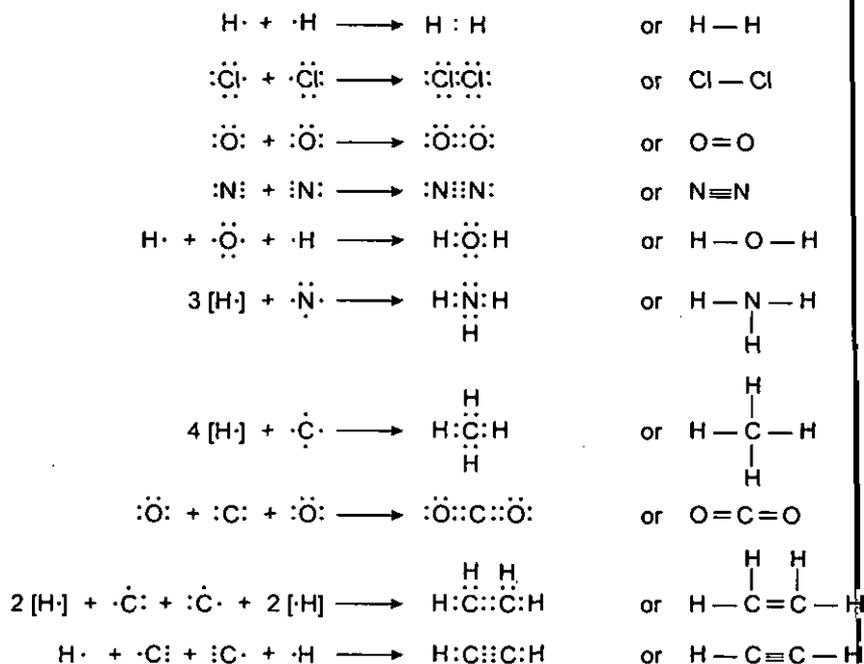
It is interesting to note that solubilities of silver halides are lower than alkali metal halides while their lattice energies are of the same order as that of alkali metal halides. This is due to the fact that silver halides undergo appreciable polarisation due to their electronic configuration ( $4s^2 4p^6 4d^{10}$ ) and hence appreciable change from ion to covalent character. On the other hand alkali metal ions are not polarised too much due to  $ns^2 np^6$  configuration.

## • 2.8. COVALENT BOND

First of all **Lewis** (1916) explained the formation of covalent bond in terms of electrons. According to Lewis the atoms (similar or dissimilar) may combine with one another by *sharing of electrons* in their valency shell to acquire the electronic configuration of nearest inert gas. Such types of bonds are known as **covalent bond** and the compounds are known as **covalent compounds**.

If similar atoms share their electron, the bond formed is called **non-polar covalent bond**. In the case of dissimilar atoms, the bond formed is termed as **polar covalent bond**. If both the atoms have been sharing one, two or three electrons each : single, double or triple covalent bonds would be formed, these bonds are represented by single line (—), two lines (=) and three lines ( $\equiv$ ) respectively.

Now we give certain examples of covalent compounds by electron dot representation (Lewis structures).



### Characteristics of Covalent Compounds

- (i) These compounds are slightly soluble in water but highly soluble in organic solvents.
- (ii) The covalent bond is generally rigid and directional hence there is possibility of position isomerism and stereo-isomerism among such compounds.
- (iii) Generally covalent compounds are gases or liquids with low boiling points. The solid covalent compounds have generally low melting points.
- (iv) Covalent compounds do not dissociate or conduct electricity.
- (v) The rate of reaction of covalent compounds are much slower as compared to ionic compounds.
- (vi) Covalent compounds, generally, form three types of crystals such as (a) in which the molecules are held by van der Waal's forces e.g., sulphur, phosphorus, pentoxide, iodine etc. (b) in which a giant molecule is formed e.g., silicon carbide, diamond etc. and (c) in which separate lattice layers are formed e.g., graphite etc.
- (vii) These compounds are soft, non-brittle and waxy due to weak forces.

**Covalency :** According to Lewis, the number of electrons that an atom contributes for sharing in a covalent bond is known as its covalency. As shown above the covalency of H, Cl, O, N and C is 1, 1, 2, 3 and 4 respectively.

### Variable Covalency

Generally the covalency of an element is equal to number of unpaired electrons present in *s*- and *p*-orbitals in its valency shell in ground state. But the elements which contain *d*-orbitals in their valence shell configurations (S, P, Cl, Br etc.) show variable covalency. Because these elements get excited, the paired electrons of *p*-orbitals become unpaired and one or more electrons shift to *d*-orbitals. Sometimes even paired electrons of *s*-orbitals become unpaired and such elements exhibit more than one covalency. For example, phosphorus forms  $\text{PCl}_3$  and  $\text{PCl}_5$  (covalency 3 and 5), sulphur forms  $\text{SCl}_2$ ,  $\text{SCl}_4$ ,  $\text{SF}_6$  (covalency 2, 4, 6), chlorine forms different covalent compounds with covalency 1, 3, 5 and 7 etc. The variable covalency of the elements of 3rd and higher periods is due to increase of number of unpaired electrons (*n*) due to different excited states.

P-atom in ground state	3s ↑↓	3p ↑ ↑ ↑	3d □ □ □ □ □	( $n = 3$ ; covalency = 3)
P-atom in 1st excited state	↑	↑ ↑ ↑	↑ □ □ □ □	( $n = 5$ ; covalency = 5)
S-atom in ground state	↑↓	↑↓ ↑ ↑	□ □ □ □ □	( $n = 2$ ; covalency = 2)
S-atom in 1st excited state	↑↓	↑ ↑ ↑	↑ □ □ □ □	( $n = 4$ ; covalency = 4)
S-atom in 2nd excited state	↑	↑ ↑ ↑	↑ ↑ □ □ □	( $n = 6$ ; covalency = 6)
Cl-atom in ground state	↑↓	↑↓ ↑↓ ↑	□ □ □ □ □	( $n = 1$ ; covalency = 1)
Cl-atom in 1st excited state	↑↓	↑↓ ↑ ↑	↑ □ □ □ □	( $n = 3$ ; covalency = 3)
Cl-atom in 2nd excited state	↑↓	↑ ↑ ↑	↑ ↑ □ □ □	( $n = 5$ ; covalency = 5)
Cl-atom in 3rd excited state	↑	↑ ↑ ↑	↑ ↑ ↑ □ □	( $n = 7$ ; covalency = 7)

### Wave Mechanical Treatment of Covalent Bond

Actually speaking treatment of the covalent bond is far more difficult than treatment of the electrovalent bond, because here we have to understand

- What type of forces exist which keep the electron pair in contact with the two atoms ?
- What is the bond energy ?
- What is geometry of the covalent compound ?
- How the electrons are arranged ?
- Why covalent bond is formed ?

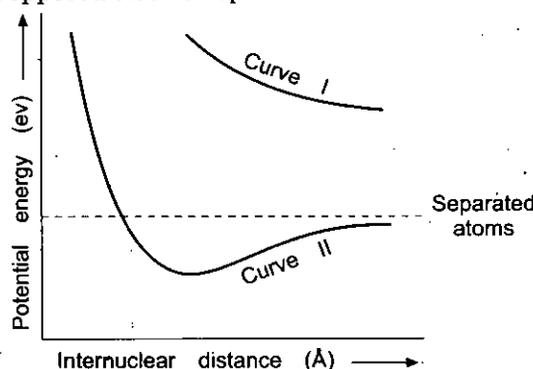
The answer of such questions may be given by Wave Mechanical Treatment of Covalent Bond. This is based on :

- Valence Bond Theory (V.B.T.)
- Molecular Orbital Theory (M.O.T.)

### • 2.9. VALENCY BOND THEORY

According to Lewis concept, a covalent bond is formed by the mutual sharing of electrons between the two atoms. This concept could not explain the nature of forces which hold the two atoms together in a covalent molecule. In order to explain the nature of these forces, Heitler and London in 1927 put forwarded valency bond theory which was later on extended by Pauling and Slater in 1931. This theory is based upon the pairing and resultant neutralization of opposed electron spins. Heitler and London calculated the energy of two interacting hydrogen atoms when they are brought from large distance to form a hydrogen molecule. The energy curves so obtained may be represented as in Figure.

The spin of the electrons of two hydrogen atoms may be in the same direction, i.e.,  $H(\uparrow)$  and  $H(\uparrow)$  or in the opposite directions,  $H(\uparrow)$  and  $H(\downarrow)$ . When two hydrogen atoms having similar spin of their electrons are brought nearer to one another, the potential energy of the



system increases as shown by curve I. This is due to the strong repulsive forces between the electrons of similar spin. When two hydrogen atoms having opposite spin electrons are brought nearer to one another, the potential energy of the system decreases as shown by curve II. As the distance between the two atoms decreases, the force of attraction increases and ultimately a critical internuclear distance is reached at which the potential energy of the system is minimum. On further decreasing the internuclear distance, the potential energy of the system again increases. This is because at such short distances, the forces of repulsion between two nuclei predominate and the molecule becomes unstable. The dissociation energy of  $H_2$  molecule is 103.2 kcal/mole, i.e., it is the energy required to dissociate  $H_2$  molecule into atoms. Thus, it is evident that the same amount of energy will be released when the bond is formed between two hydrogen atoms. The minima in curve II shows bond formation.

At critical internuclear distance, the electron of one atom moves to the other atom and vice versa, i.e., an exchange of electrons may take place. Each electron has an equal possibility of being found on either atom and each nucleus may be associated with both electrons. Thus, it is not possible to distinguish the two electrons after the bond formation, i.e., it cannot be said as to which electron belongs to which atom. Due to exchange of electrons, the exchange forces develop which further stabilize the molecule.

The formation of a stable bond between two atoms having electrons of opposite spin is also in accordance with Pauli's exclusion principle. Each electron possesses a magnetic dipole because of its spin. When the spin of two electrons is opposite in an orbital, the mutual neutralization of dipole moments results in an attractive force which is responsible for holding the atoms together in a molecule. According to the orbital overlap concept, a covalent bond is formed by the overlapping of atomic orbitals. As a result, there is an increase in the electron density wherever overlapping occurs, i.e., at the midpoint between the two atoms. Thus, the electrostatic attraction between the nuclei and accumulated electron cloud is responsible for holding the atoms together in a molecule.

The theory can be extended to other molecules if their atoms have unpaired electrons. If the electrons are not unpaired in the ground state, there must be vacant orbitals of slightly higher energy of the same main energy level to accommodate the previously paired electrons in the separate orbitals. The energy needed to unpair the electrons is utilized from the energy released when a covalent bond is formed. Thus, nitrogen with outer configuration  $2s^2 2p_x^1 2p_y^1 2p_z^1$  can form only three bonds as  $NCl_3$ . Nitrogen cannot form  $NCl_5$  as it does not have vacant  $d$ -orbitals to accommodate one of the unpaired  $2s$  electrons. On the other hand, phosphorus with an outer configuration  $3s^2 3p_x^1 3p_y^1 3p_z^1$  can form  $PCl_5$  also as phosphorus atom has vacant  $d$ -orbitals to accommodate one of the unpaired  $3s$  electrons.

**Limitations of valency bond theory :** This theory does not explain :

- (i) The formation of co-ordinate bond in which shared pair of electrons is contributed by only one of the combining atoms.
- (ii) The paramagnetic nature of oxygen molecule.
- (iii) The structure of odd electron molecules or ions where no pairing of electrons takes place.
- (iv) The directional nature of covalent bond.
- (v) The formation and structure of several compounds involving resonance and hybridization.

**Pauling-Slater Theory :** Pauling and Slater (1931) accepted the essential feature of Heitler-London theory and they extended it to make it more general and also to account for the directional nature of covalent bonds. According to this theory :

- (i) The greater the overlapping of atomic orbitals, the greater will be the strength of the bond formed. Thus, the strength of the bond is directly proportional to the extent of overlapping of the two atomic orbitals.

(ii) The overlapping takes place between orbitals of only those electrons which are involved in the bond formation, *i.e.*, outermost orbitals containing valency electrons.

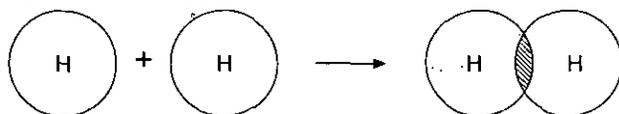
(iii) The *s*-orbital is spherically symmetrical, *i.e.*, its electron density is uniformly distributed around the nucleus. When such an orbital is involved in the bond formation, the electrons will not show any directional preference.

(iv) The electron density of all other orbitals is directed in certain specified direction in space. For example, in the case of *p*-orbitals it is directed towards the three axes, *i.e.*, X, Y and Z. These orbitals will form a bond in the direction of greatest electron density.

(v) Of the two orbitals having same energy, the one which is more directionally concentrated will form a stronger bond. For example, dumbbell shaped *p*-orbital will form stronger bond than spherically symmetrical *s*-orbital.

### Structures of Some Molecules on the Basis of Overlapping of Atomic Orbitals :

(i) **Hydrogen molecule (*s-s* overlapping)** : The hydrogen atom has  $1s^1$  orbital and is, therefore, available for bond formation. In the formation of hydrogen molecule two *s*-orbitals overlap (*s-s* overlapping) and form a covalent bond.

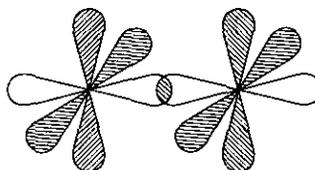


Formation of  $H_2$  molecule by *s-s* overlapping

(ii) **Fluorine molecule (*p-p* overlapping)** : The electronic configuration of fluorine is  $1s^2 2s^2 2p_x^2 2p_y^2 2p_z^1$ . In this atom one unpaired electron is present in the  $2p$  orbital. In the formation of fluorine molecule, two such orbitals overlap (*p-p* overlapping) and form a covalent bond.

The formation of  $Cl_2$  and  $Br_2$  molecules may be explained in a similar manner.

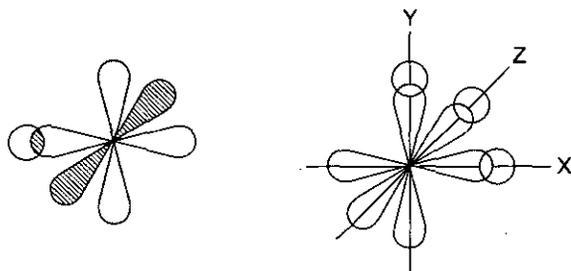
(iii) **Hydrogen fluoride molecule (*s-p* overlapping)** : The electronic configuration of hydrogen is  $1s^1$  and that of fluorine is  $1s^2 2s^2 2p_x^2 2p_y^2 2p_z^1$ . Thus, both hydrogen and fluorine have half filled *s* and *p*-orbitals. In the formation of HF molecule  $1s$  orbital of hydrogen overlaps with  $2p_z$  orbital of fluorine (*s-p* overlapping) and forms a covalent bond.



Formation of  $F_2$

The formation of  $HCl$  may be explained in similar manner.

(iv) **Ammonia molecule** : The electronic configuration of nitrogen is  $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$  and that of hydrogen is  $1s^1$ . Thus, nitrogen has three half filled *p*-orbitals and hydrogen has one half filled *s*-orbital. The nitrogen, therefore, combines with three atoms of hydrogen to form a molecule of  $NH_3$ .

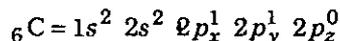


Formation of  $H-F$   
by *s-p* overlapping

Formation of  
 $NH_3$  by *s-p* overlapping

## • 2.10. HYBRIDIZATION

The formation of compounds of beryllium, boron, carbon and many other elements could not be explained simply by the concept of overlapping of atomic orbitals. For example, the electronic configuration of carbon is :

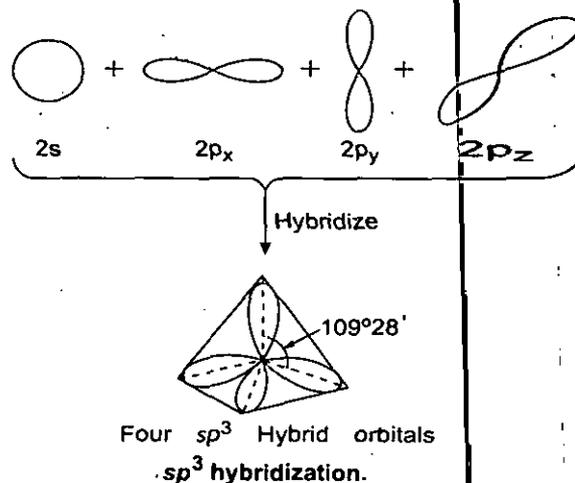


In the ground state, carbon has two unpaired electrons. Therefore, it should be divalent but it is found to be tetravalent in almost all its compounds. The tetravalency of carbon may be explained by assuming that one of the two 2s electrons is excited to vacant  $2p_z$  orbital, thus, giving the configuration as  $1s^2 2s^1 2p_x^1 2p_y^1 2p_z^1$ . Now the carbon atom has four unpaired electrons and, therefore, it can form four bonds, three of which formed by three  $p$ -orbitals will be at right angles to one another and the fourth formed by  $s$ -orbital will have no directional preference. Accordingly, the three bonds should be of one type and the fourth should be of another type. But in actual practice, all the four bonds of carbon are equivalent in all respects. To explain this, it is assumed that four atomic orbitals of carbon ( $2s, 2p_x, 2p_y$  and  $2p_z$ ) get mixed up and form four equivalent hybrids of equal energy.

The phenomenon of mixing up of atomic orbitals of similar energy and formation of equivalent number of entirely new orbitals of identical shape and energy is known as hybridization and the new orbitals so formed are called hybrid orbitals. The bonds formed by these orbitals are stronger than the bonds formed by pure  $s, p$  or  $d$ -orbitals.

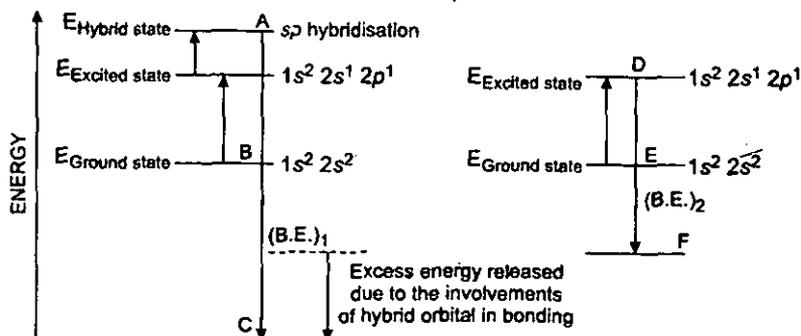
The four new bonds, thus formed are directed towards the four corners of regular tetrahedron and are inclined to each other at an angle of  $109^\circ 28'$ . The whole phenomenon may be represented as :

Since in the above case, hybridization has taken place by the combination of one  $s$  and three  $p$ -orbitals, it is called as  $sp^3$  hybridization.



### Energetics of Hybridization

When atomic orbitals combine to form hybrid orbital energy is released which provides extra stability to the molecule. Let us discuss the formation of  $\text{BeCl}_2$ . In this molecule Be is a central atom and its electronic configuration is  $1s^2 2s^2$ . Since there is no unpaired electron in Be atom hence according to VBT it should not form a molecule. But  $\text{BeCl}_2$  is formed, therefore we say that Be atom gains some energy by mixing  $2s$  and  $2p$ -orbitals to form  $sp$ -hybrid orbitals. When two half-filled hybrid orbitals overlap with  $3p$  orbitals



of chlorine energy is released and  $\text{BeCl}_2$  molecule is formed. It is illustrated in the figure given above.

Evidently energy released  $(\text{B.E.})_1$  is due to the formation of  $\sigma$ -bond between  $sp$  hybrid orbitals of Be and  $p$ -orbitals, of chlorine atoms. Energy released  $(\text{B.E.})_2$  is due to the formation of  $\sigma$ -bonds between  $s$  and  $p$ -orbitals of Be and  $p$ -orbitals of chlorine atoms. In figure  $(\text{B.E.})_1$  and  $(\text{B.E.})_2$  are represented by BC and EF respectively.

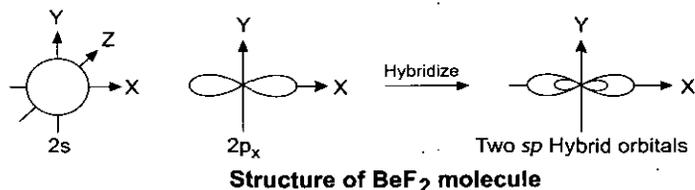
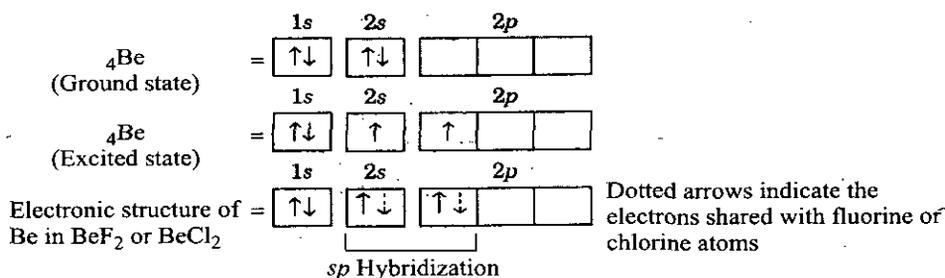
Since some addition energy is released due to the involvement of the  $sp$  hybrid orbitals of Be-atom in bond formation hence these bonds are stronger than the bonds formed by pure  $s$ - and  $p$ -orbitals of Be atom.

In the same way we can explain the energetics of hybridization of different hybrid orbitals such as  $sp^2$ ,  $sp^3$ ,  $dsp^2$ ,  $d^2sp^3$  etc.

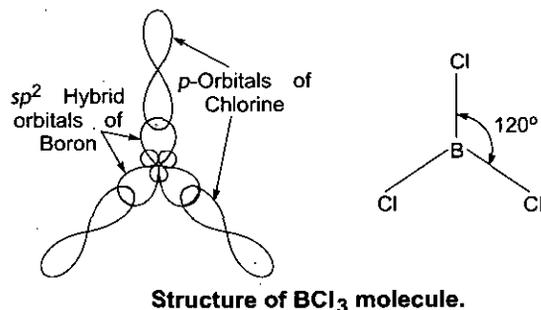
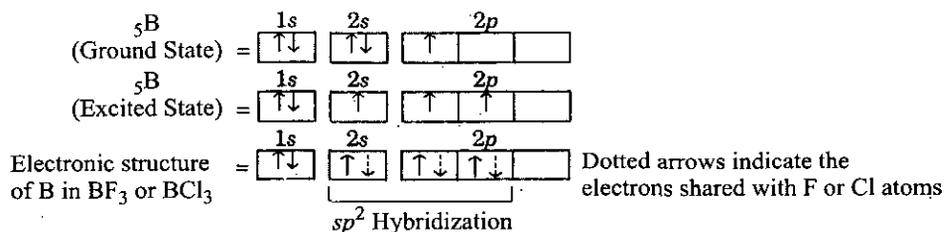
### Types of hybridization and shapes of covalent molecules

(i)  **$sp$ -Hybridization** : The combination of one  $s$  and one  $p$ -orbital to form two hybrid orbitals of equal energy is known as  $sp$  hybridization. This type of hybridization is found in beryllium compounds like  $\text{BeF}_2$ ,  $\text{BeCl}_2$  etc.

The molecules involving this type of hybridization are linear with a bond angle of  $180^\circ$ . Other common examples of  $sp$ -hybridization are  $\text{CO}_2$ ,  $\text{HgCl}_2$ ,  $\text{C}_2\text{H}_2$  etc.

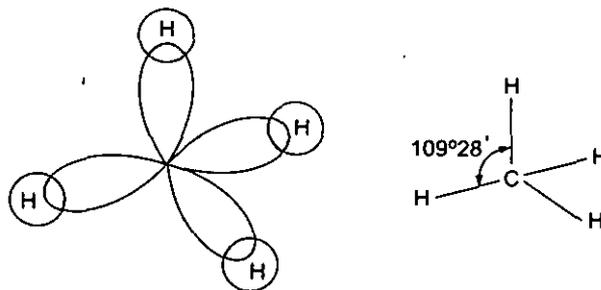
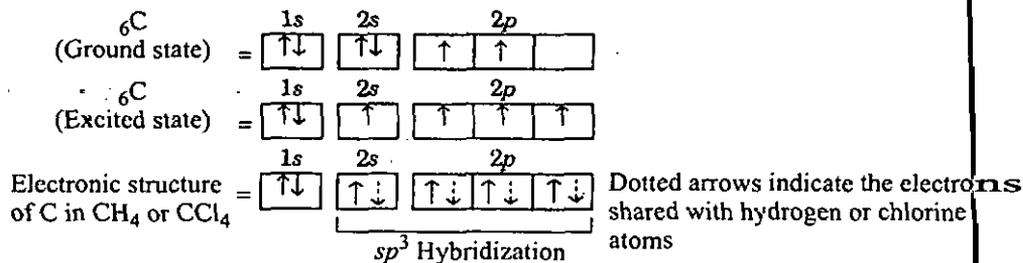


(ii)  **$sp^2$ -Hybridization** : The combination of one  $s$  and two  $p$ -orbitals to form three hybrid orbitals of equal energy is known as  $sp^2$ -hybridization. This type of hybridization is found in boron compounds like  $\text{BF}_3$ ,  $\text{BCl}_3$  etc.



The molecules involving this type of hybridization are plane triangular with a bond angle of  $120^\circ$ . Other common examples of  $sp^2$  hybridization are  $SO_2$ ,  $C_2H_4$ ,  $CO_3^{3-}$ ,  $NO_3^-$  benzene etc.

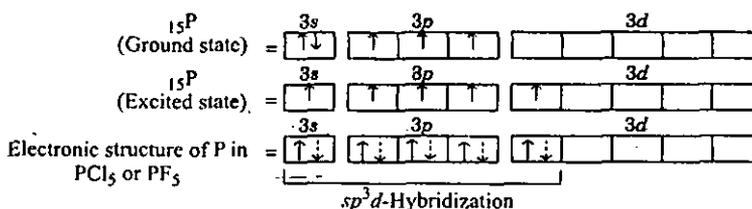
(iii)  $sp^3$ -Hybridization : The combination of one  $s$  and three  $p$  orbitals to form four hybrid orbitals of equal energy is known as  $sp^3$ -hybridization. This type of hybridization is found in carbon compounds like  $CH_4$ ,  $CCl_4$ ,  $CH_3OH$  etc.



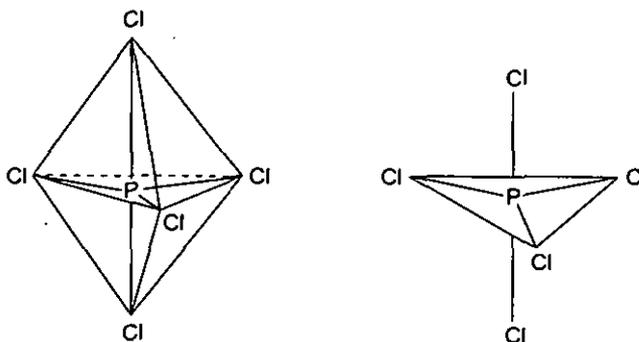
Structure of  $CH_4$  molecule.

The molecules having this type of hybridization are tetrahedral with a bond angle of  $109^\circ 28'$ . Other common examples of  $sp^3$  hybridization are  $SiH_4$ ,  $SiF_4$ ,  $SiCl_4$ ,  $NH_3$ ,  $H_2O$  etc.

(iv)  $sp^3d$ -Hybridization : The combination of one  $s$ , three  $p$  and one  $d$ -orbitals to form five hybrid orbitals of equal energy is known as  $sp^3d$  hybridization. An example is the structure of  $PCl_5$ ,  $PF_5$  etc.



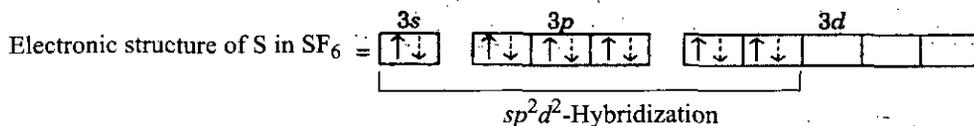
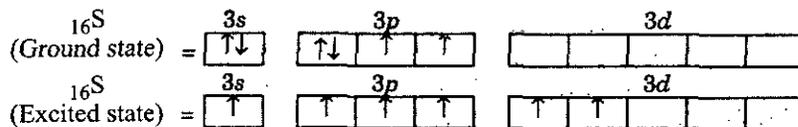
(Dotted arrows indicate the electrons shared with chlorine or fluorine atoms).



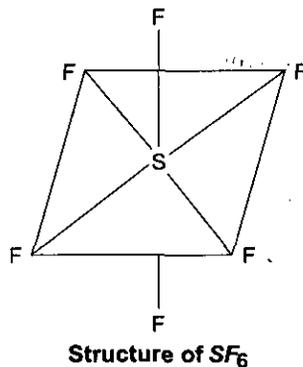
Structure of  $PCl_5$

The molecules having this type of hybridization are trigonal bipyramidal in shape having bond angle  $120^\circ$  and  $90^\circ$ .

(v)  $sp^3d^2$  Hybridization: The combination of one  $s$ , three  $p$  and two  $d$ -orbitals to form six hybrid orbitals of equal energy is known as  $sp^3d^2$  hybridization. An example is the structure of  $SF_6$ .

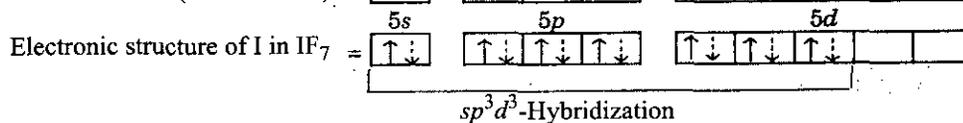
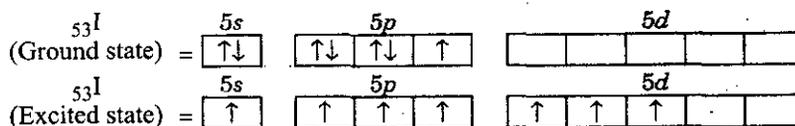


(Dotted arrows indicate the electrons shared with fluorine atoms).

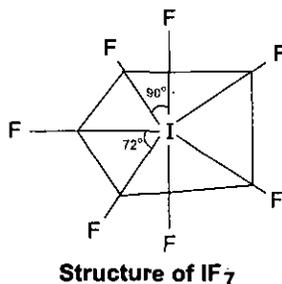


The molecules having this type of hybridization are octahedral in shape having a bond angle of  $90^\circ$ .

(vi)  $sp^3d^3$  Hybridization: The combination of one  $s$ , three  $p$  and three  $d$ -orbitals to form seven hybrid orbitals of equal energy is known as  $sp^3d^3$  hybridization. An example is the structure of  $IF_7$ .



(Dotted arrows indicate the electrons shared with F atoms).



The molecules having this type of hybridization are pentagonal bipyramidal in shape with a bond angle  $72^\circ$  and  $90^\circ$ .

### Bent's Rule

According to hybridization atomic orbitals combine and redistribute their energies to form hybrid orbitals. These are identical w.r.t. energy shape etc. Shapes of the hybrid orbitals depends upon the contribution of  $s$ ,  $p$ -orbitals.

In the case of  $sp^3$ -hybridisation,  $CH_4$  or  $CCl_4$  shows tetrahedral geometry with bond angle  $109^\circ 28'$ . But in the case of  $CH_2F_2$ , the  $F-C-F$  bond angle is less, this may be explained with the help of Bent's rule.

**Bent's rule** states that, 'More electronegative substituents prefer hybrid orbital having less s-character and more electropositive substituents prefer hybrid orbital having more s-character.'

This is the reason that in  $F-C-F$  s-character is less than 25% while in  $H-C-H$  it is more than 25%.

In trigonal bipyramidal structures, the tendency of more electronegative substituents to seek out the low electronegative  $p_z, d_{z^2}$  apical orbital (i.e., apex orbital) is known as 'apicophilicity'.

It is interesting to note that in the formation of  $PCl_5$ , P-atom exhibits  $sp^3d$  hybridization in which three hybrid orbitals are on the plane and two hybrid orbitals are above and below the plane. In this  $p_z d_{z^2}$  form linear hybrid orbitals axially and  $s p_x p_y$  form trigonal equatorial bonds. Evidently P-Cl bonds which are on the axis are longer (i.e., lesser bond energy) than equatorial. But in the case of  $PCl_3F_2$ , it is observed that P-F bonds are on the axis and P-Cl bonds are on the equatorial. This is according to Bent's rule, because F-atom is more electronegative hence prefer less s-character and is on the axis ( $p_z d_{z^2}$ ) while Cl-being less electronegative prefer more s-character ( $s p_x p_y$ ).

If we consider the case of  $PF_5$  in which P-atom exhibits  $sp^3d$  hybridization which may be considered to be a combination of  $p_z d_{z^2}$  hybrids (which forms two linear hybrid orbitals bonding axially) and  $s p_x p_y$  hybrids (which forms the trigonal, equatorial bonds). The bond lengths in  $PF_5$  are 153.4 pm and 157.7 pm for equatorial bonds ( $r_{eq}$ ) and axial bonds ( $r_{ax}$ ) respectively. It clearly indicates that equatorial bonds are stronger than axial bonds. In other words, energy of equatorial bonds is higher than that of axial bonds. Similarly we can explain the other examples of the type  $MX_5$  ( $M = P, As, Sb, Bi$  and  $X = Cl, Br, I$ ).

## • 2.11. RESONANCE

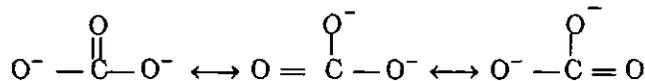
It may be defined as :

(i) Resonance involves canonical forms in which certain atoms are required to bear unit charges. These charges are termed formal charges and their calculation is based upon the number of electrons in valency shell of the atom (shared electrons counts as one-half of a unit negative charge).

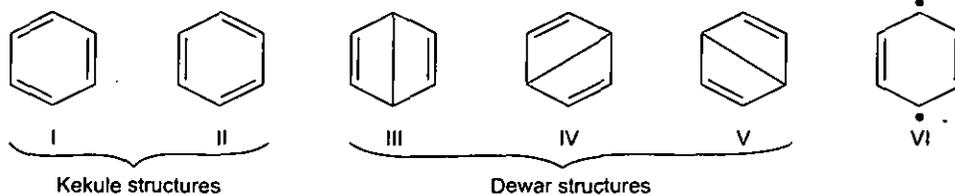
(ii) Resonance is the description of the electronic structure of molecule (ion) by means of several schemes of pairing electrons, with features of each scheme contributing to final description.

### Principles of Resonance

(i) Position of the atoms in a molecule (ion) should remain the same, electron may be changed.



(ii) Resonance is particularly important when the contributing structures are of about the same stability. For example structures I and II are the resonating structures of benzene. Because other structures have different stabilities.



(iii) The number of unpaired electrons in each contributing structure must be the same, therefore structure VI for benzene is not accepted.

(iv) The more stable is a contributing structure the greater will be its contribution to the resonance hybrid.

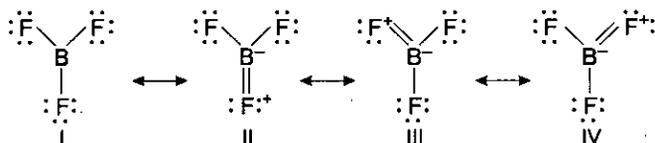
(v) The resonance hybrid is more stable than any of the contributing structure. The difference in energies is known as **resonance energy**.

(vi) The greater is the number of contributing structures that can be written for a molecule, the more stable it would be.

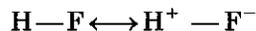
(vii) In resonating structure atoms should not undergo appreciable shift (**Tautomerism**).

(viii) Resonating structures must have nearly the same energy. Structures which have very high energy do not contribute, lower the energy greater the contribution.

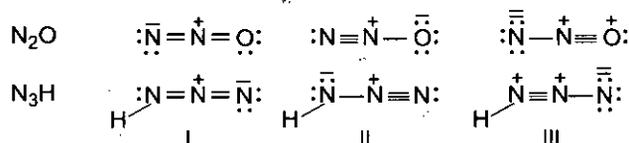
(a) Structures having lesser number of covalent bonds have higher energy i.e., lesser stability. For example, for  $\text{BF}_3$  the structure I is less stable while structure II is more stable, due to the increase of bond by one. It has 54%  $\pi$  character.



(b) Structures with unfavourable charge distribution do not coincide. For example in HF molecule  $\text{H}^- \text{F}^+$  resonating structure is not possible. Hence the resonance will be in the following structures:

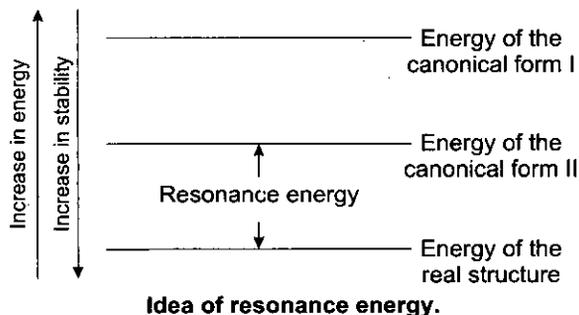


(c) If adjacent atoms have the same charge structures do not contribute. For example



In both the cases structures III are not possible,

(ix) The canonical form should be of similar energies because a relatively very high energy form is not expected to contribute much towards resonance.



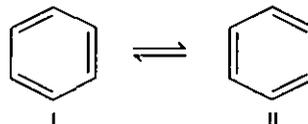
(x) The relative position of various atoms involved must remain unchanged in all canonical forms,

### Properties of Resonance Hybrid

(i) **Heat exchange** : The observed heat of formation of a resonance hybrid is more than that calculated for any discrete structure. For example,

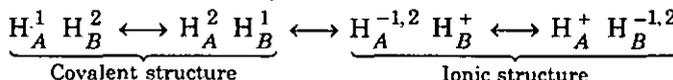
the observed heat of formation of  $\text{CO}_2$  is greater than calculated value (for structure  $\text{O}=\text{C}=\text{O}$ ) by 31.6 kcal. In other words, actual  $\text{CO}_2$  is more stable than expected on the basis of discrete structure,  $\text{O}=\text{C}=\text{O}$ . Such a difference in observed value and calculated value of heats of formation is generally called as resonance energy. This idea can be represented as shown in the Figure. Hence we conclude that greater the resonance energy of a molecule the more stable it would be. Thus stability is directly proportional to resonance energy.

(ii) **Bond lengths** : It is also seen that bond lengths in molecule showing resonance are different from those expected on the basis of discrete structure. For example in benzene (structure I or II); this will require the presence of two types of carbon-carbon bonds and these bonds should have lengths of 1.54 Å and 1.33 Å. Actually carbon-carbon bonds of benzene are equal and have a length of 1.397 Å, intermediate between lengths of single and double bonds. Such bonds are generally called as hybrid bonds.



**Examples :**

(i)  **$\text{H}_2$  molecule** : Let there be two hydrogen atoms as  $A$  and  $B$  associated with electrons 1 and 2 respectively. Its resonance forms are given below :



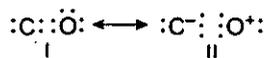
(ii)  **$\text{CO}$  molecule** : In ground state, carbon atom has two unpaired electrons ( $2p_x^1 2p_y^1$ ) hence the structure of carbon monoxide can be written as  $\text{C}=\text{O}$ . But this structure is not tenable on the following basis :

(a) **Bond length** : The measured bond length between carbon and oxygen is 1.13 Å which is intermediate between double bond (1.22 Å) and triple bond (1.10 Å) in carbon and oxygen atoms.

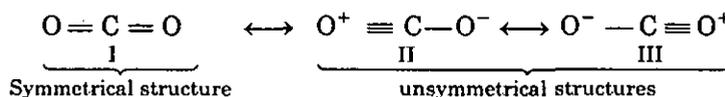
(b) **Bond energy** : The calculated bond energy is 173 kcal  $\text{mol}^{-1}$  whereas measured value is 256 kcal  $\text{mol}^{-1}$  for  $\text{CO}$  molecule. This difference of 83 kcal  $\text{mol}^{-1}$  represents resonance energy.

(c) **Dipole moment** : The dipole moment is very very small while according to its structure given above, it must show an appreciable value of dipole moment.

Hence  $\text{CO}$  is a resonance hybrid of I and II

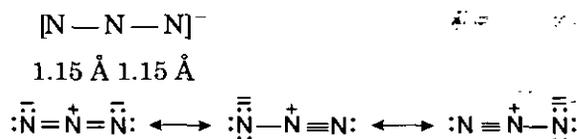


(iii)  **$\text{CO}_2$  molecule** : On the basis of classical model of atom,  $\text{CO}_2$  is represented as  $\text{O}=\text{C}=\text{O}$ . This structure is supported by dipole moment value i.e., zero. But resonance energy and bond length, as discussed above, do not agree with this structure hence the following resonance hybrids are given as :



The dipole moment for the structures II and III is again zero due to opposite directions.

(iv)  $\text{N}_3^-$  (Azide) ion : Azide ion is linear and symmetrical with bond distance  $1.15 \text{ \AA}$  from the central atom. This is compatible with resonance among the following three structures :



Some more examples are given in the following Table :

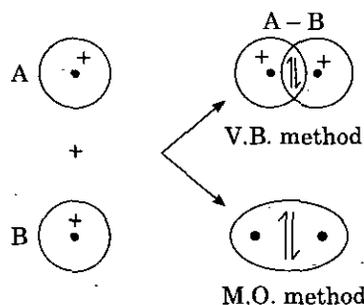
Molecule or Ion	General Geometry	Resonance forms*
1. $\text{NO}_2$	Bent	
2. $\text{NO}_3^-$	Planar	
3. $\text{CO}_3^{2-}$	Planar	
4. $\text{SO}_4^{2-}$	Tetrahedral	
5. $\text{CH}_3\text{COO}^-$	—	
6. $\text{C}_2\text{H}_5\text{NO}_2$	—	

## • 2.12. MOLECULAR ORBITAL THEORY

Hund and Mullikan (1930) developed an approach to bond formation.

According to this theory the atomic orbitals combine and form a resultant orbital known as the *molecular orbital* in which the identity of both the atomic orbitals is lost. All the electrons pertaining to both the atoms are considered to be moving along the entire molecule under the influence of all the nuclei.

This may be illustrated by the figure depicted here.



Formation of AB molecule by valence bond method and molecular orbital method

### Basic Principles of MOT

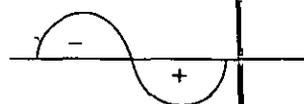
1. When nuclei of two atoms come close to each other, their atomic orbitals interact resulting in the formation of molecular orbitals (M.O.). In a molecule atomic orbitals of atoms lose their identity after the formation of molecular orbitals.
2. Each M.O. may be described by the wave function  $\psi$ , which is known as M.O. wave function.  $\psi^2$  represents the probability density or electron density.
3. Each M.O. wave function ( $\psi$ ) is associated with a set of quantum number which represents the energy and shape of the occupied M.O.
4. Each  $\psi$  is associated with a definite energy value. The total energy of the molecule is the sum of the energies of the occupied M.O.
5. Electrons tend to fill the M.O. in the same way, as they filled in the atomic orbitals following the Aufbau principle, Hund's rule and Pauli's exclusion principle.
6. Each electron in a M.O. belongs to all the nuclei present in the molecule.
7. Each electron moving in the M.O. is having clockwise or anticlockwise (i.e.  $+\frac{1}{2}$  or  $-\frac{1}{2}$ ) spin.

### Comparison between Atomic and Molecular Orbitals

Atomic Orbitals		Molecular Orbitals	
1.	They belong to a particular atom and are influenced by one nucleus i.e. monocentric.	1.	They belong to the whole molecule (or ion) and are influenced by more than one nucleus i.e. polycentric.
2.	They are denoted by <i>s, p, d, f</i> etc.	2.	They are denoted by $\sigma, \sigma^*, \pi, \pi^*, \delta, \delta^*$ etc.
3.	They have definite shapes.	3.	They do not have definite shapes.
4.	They can accommodate a maximum two electrons of opposite spins.	4.	They can also accommodate a maximum two electrons of opposite spin.

### Salient Features of Molecular Orbital Theory

(i) When two isolated atomic orbitals (A.Os.) (or their wave function) of two atoms having similar energy and symmetry combine linearly with each other by linear combination of atomic orbital (LCAO)



Representation of electron wave

method (described below) two M.Os. are obtained. If both the atoms are of the same element that is called homo-nuclear diatomic molecule or ion (e.g.  $H_2, H_2^+, H_2^-, N_2, O_2, O_2^+, O_2^-$  etc.). If both the atoms are of the different elements, that is called hetero-nuclear diatomic molecule or ion (e.g. CO, NO, HF,  $CN^-, NO^+, NO^-$  etc.)

When three A.Os. of similar energy and same symmetry combine with one another, three M.Os. are obtained.

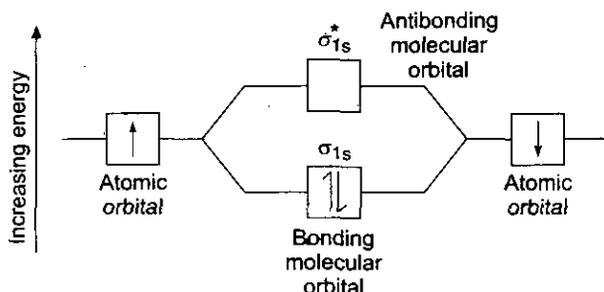
Therefore, it may be concluded that number of M.Os. obtained is always equal to number of A.Os. combining together.

(ii) **Linear Combination of Atomic Orbitals (LCAO):** The molecular orbitals can be obtained by the method of LCAO. Let two atoms *A* and *B* form *AB* molecule (hetero-diatom molecule). Their A.Os. are represented by  $\psi_A$  and  $\psi_B$  respectively. There are following two ways of their combination.

(a) **Additive overlap:** It is also known as positive overlap or ++ overlap. In this type of linear combination, the positive lobe (i.e. the lobe having + sign) of  $\psi_A$  overlaps with the positive lobe of  $\psi_B$  thus a molecular orbital is formed. This molecular orbital

has lower energy than that of atomic orbitals of atoms  $A$  and  $B$  due to attraction between the nuclei of  $A$  and  $B$ . Such type of molecular orbitals are known as **bonding molecular orbitals (BMO)** and represented as  $\psi^b$ .

(b) **Subtractive overlap**: It is also known as *negative overlap* or *+– overlap*. In this type of linear combination, the positive lobe of  $\psi_A$  overlaps with the negative lobe (*i.e.* the lobe having – sign) of  $\psi_B$  thus a molecular orbital is formed. This molecular orbital has higher energy than that of atomic orbitals of atoms  $A$  and  $B$  due to repulsion between the nuclei of  $A$  and  $B$ . Such type of molecular orbitals are known as **anti bonding molecular orbitals (ABMO)** and represented as  $\psi^a$  or  $\psi^*$ .



Formation of bonding and anti-bonding molecular orbitals.

#### Differences between BMO and ABMO

BMO		ABMO	
1.	These are formed by the addition of the orbitals of same phase <i>i.e.</i> , $\psi = \psi_A + \psi_B$ .	1.	These are formed by the subtraction of the orbitals of same phase or addition of the orbitals of different phase <i>i.e.</i> , $\psi = \psi_A - \psi_B$ .
2.	They have lower energy than atomic orbitals involved.	2.	They have higher energy than atomic orbitals involved.
3.	Electron charge density increases between the nuclei involved thus stability of the molecule increases.	3.	Electron charge density decreases between the nuclei involved thus stability of the molecule decreases.

**Pictorial Representation of Combination of Atomic Orbitals to form Molecular Orbitals**: Here we discuss the combination of different atomic orbitals  $s$ - and  $p$ -orbitals as follows:

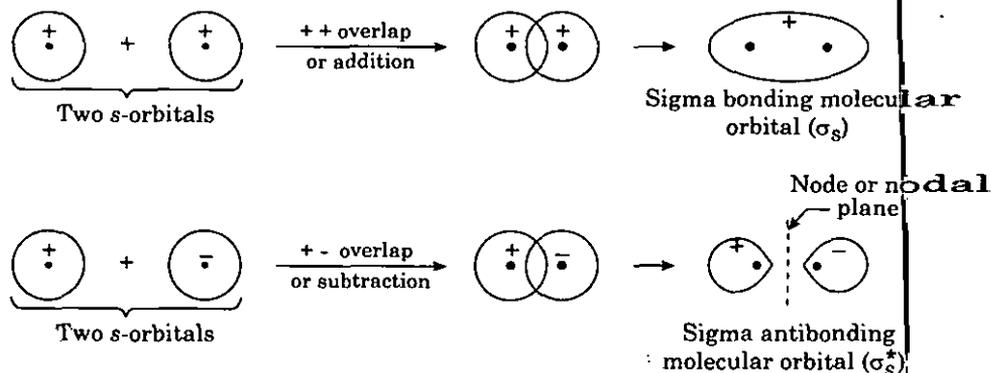
(i) **Combination of  $s$ -orbitals**: When two  $s$ -orbitals overlap with each other we get two molecular orbitals known as BMO and ABMO. Obviously first one is due to *additive combination* (or *++ overlap*) and second one is due to *subtractive combination* (or *+– overlap*). In *++ overlap* the electron charge density in the region between the two nuclei would get intensified.

Thus high charge density in between the two nuclei shields them from mutual repulsion and holds them together at the observed distance from each other while in *+– overlap* the electron charge density would get removed from the middle of the two nuclei. Thus there will be no shielding of the nuclei or repulsion between two nuclei would be increased thereby increasing the energy of the molecular orbital formed.

If  $1s$  atomic orbitals overlap with each other, the BMO is represented as  $\sigma(1s)$  orbital. The sign  $\sigma$  signifies that the orbital is *symmetrical about the molecular axis* and the script  $(1s)$  indicates that it is formed by the combination of  $1s$  atomic orbitals, while ABMO is designated as  $\sigma^*(1s)$ .

In the same way if  $2s$  or  $3s$  atomic orbitals combine to form BMO and ABMO, these will be designated by  $\sigma(2s)$  and  $\sigma^*(2s)$  or  $\sigma(3s)$  and  $\sigma^*(3s)$ .

The formation of  $\sigma(s)$  and  $\sigma^*(s)$  molecular orbitals are shown in the following figure.

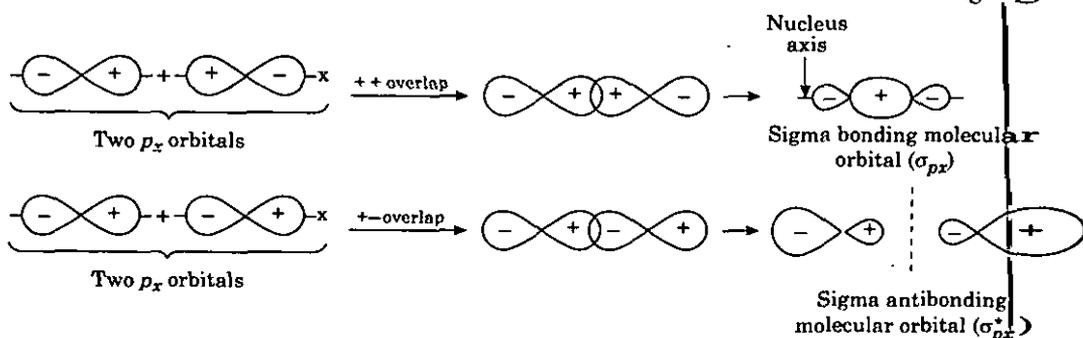


Formation of  $\sigma(s)$  molecular orbitals by  $++$  and  $+ -$  overlap of two  $s$ -orbitals

(ii) **Combination of  $p$ -orbitals:** There are three  $p$ -orbitals ( $p_x$ ,  $p_y$  and  $p_z$ ) in  $p$ -sub-shell. These can overlap and can combine either end to end to give  $\sigma$ -molecular orbitals or side to side (sidewise) to give  $\pi$ -molecular orbitals. Here both types of combinations are described.

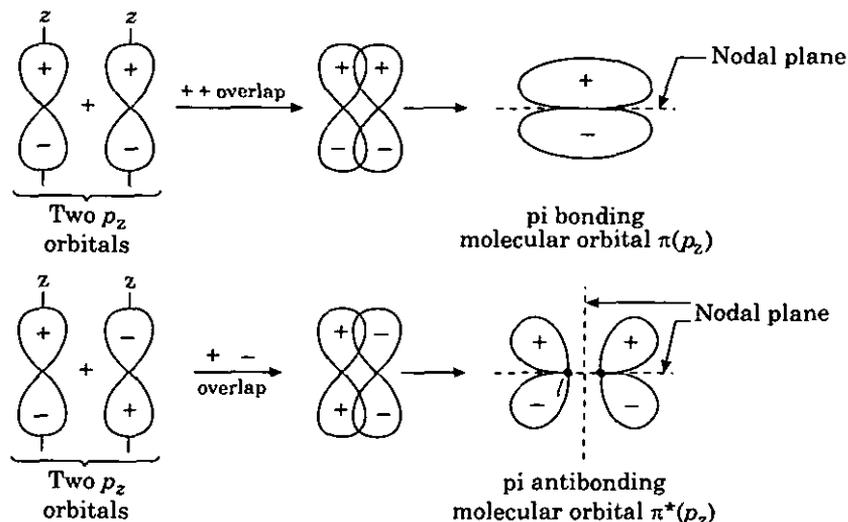
(a) **Combination of  $p_x$  orbitals:** Let  $x$ -axis be the molecular axis. Therefore when two  $p_x$  atomic orbitals overlap on  $x$ -axis, then two sigma molecular orbitals are formed.

One of these is sigma BMO [i.e.  $\sigma(p_x)$ ] having lower energy (due to  $++$  overlap) than that of  $p_x$ -atomic orbitals and the other is sigma ABMO [i.e.  $\sigma^*(p_x)$ ] having higher energy (due to  $+ -$  overlap) than that of  $p_x$ -atomic orbitals. The sigma  $\sigma_{p_x}$  etc. signifies as above. The formation of these molecular orbitals are shown in the following figure.



Formation of  $\sigma(p_x)$  and  $\sigma^*(p_x)$  molecular orbitals by  $++$  and  $+ -$  overlap of two  $p_x$  orbitals

(b) **Combination of  $p_y$  or  $p_z$  orbitals:** Since  $x$ -axis is considered as molecular axis hence  $y$ - and  $z$ -axes are perpendicular to molecular axis. When two



Formation of  $\pi(p_z)$  and  $\pi^*(p_z)$  molecular orbitals by  $++$  and  $+ -$  overlap of two  $p_z$  orbitals

$p_y$  or  $p_z$  orbitals overlap together along the molecular axis (i.e.  $x$ -axis) two pi molecular orbitals are formed. One of these is pi BMO [i.e.  $\pi(p_y)$  or  $\pi(p_z)$ ] having lower energy (due to  $++$  overlap) than that of  $p_y$  or  $p_z$  atomic orbitals and the other is pi ABMO [i.e.  $\pi^*(p_y)$  or  $\pi^*(p_z)$ ] having higher energy (due to  $+ -$  overlap). The sign  $\pi$ ,  $p_y$  or  $p_z$  etc. signifies as above. The formation of these molecular orbitals is shown above.

Similarly we can show the formation of  $\pi(p_y)$  and  $\pi^*(p_y)$  molecular orbitals.

**Bond order :** The bond order (B.O.) in diatomic molecules is half of the difference between the total number of the bonding electron ( $N_b$ ) and antibonding electrons ( $N_a$ ). Therefore

$$\text{B.O.} = \frac{N_b - N_a}{2}$$

As the bond order increases *stability of the bond increases and bond length decreases*.

If bond order is zero, the molecule does not exist. If bond order is 0.5, the atoms of the molecule are linked by one electron only e.g.,  $\text{H}_2^+$  it may be written as  $[\text{H} \cdot \text{H}]^+$ . The bond order of  $\text{H}_2^-$  and  $\text{He}_2^+$  is also 0.5, but in this case there are three electrons therefore they may be represented as  $[\text{H} \cdots \text{H}]^-$  and  $[\text{He} \cdots \text{He}]^+$  respectively. If bond order is 1.5 or 2.5 it indicates that one bond is formed by three electrons e.g.,  $\text{O}_2^-$  may be written as  $[:\ddot{\text{O}} \cdots \ddot{\text{O}}:]^-$  (B.O. 1.5). The ions  $\text{N}_2^+$  and  $\text{O}_2^+$  both have B.O. 2.5 and may be written as  $[\text{N} \equiv \text{N}]^+$  and  $[:\text{O} \equiv \text{O}:]^+$  respectively.

**Magnetic Properties :** The species (molecule or ion) which have unpaired electrons are *paramagnetic* while those have paired electrons are *diamagnetic*. The magnetic moment ( $\mu_{\text{eff}}$ ) is related with number of unpaired electrons as :

$$\mu_{\text{eff}} = \sqrt{n(n+2)} \text{ B.M.}$$

where  $n$  is number of unpaired electrons.

### Energy Level Diagram for Molecular Orbitals

The energy level of these orbitals have been determined experimentally from spectroscopic data. The order of their increasing energy is given below and shown in the figure.

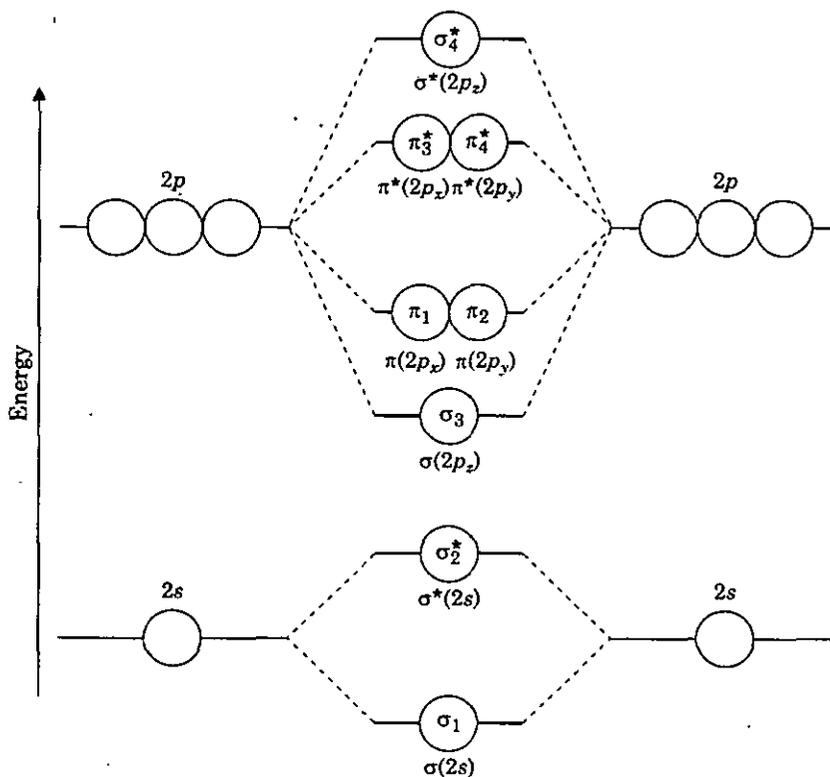
The electrons in the molecular orbitals are filled in the following order :

$$\begin{aligned} \sigma(1s) < \sigma^*(1s) < \sigma(2s) < \sigma^*(2s) < \sigma(2p_z) < \pi(2p_x) = \pi(2p_y) \\ < \pi^*(2p_x) = \pi^*(2p_y) < \sigma^*(2p_z) \end{aligned}$$

According to **recent convention**, the M. Os. such as  $\sigma(2s)$ ,  $\sigma^*(2s)$ ,  $\sigma(2p_z)$ ,  $\sigma^*(2p_z)$  etc. are written as  $\sigma_1$ ,  $\sigma_2^*$ ,  $\sigma_3$ ,  $\sigma_4^*$  where as M. Os.  $\pi(2p_x)$ ,  $\pi(2p_y)$ ,  $\pi^*(2p_x)$ ,  $\pi^*(2p_y)$  are written as  $\pi_1$ ,  $\pi_2$ ,  $\pi_3^*$ ,  $\pi_4^*$  as shown in the figure (page 64). This new convention is particularly useful for heteronuclear molecules or ions.

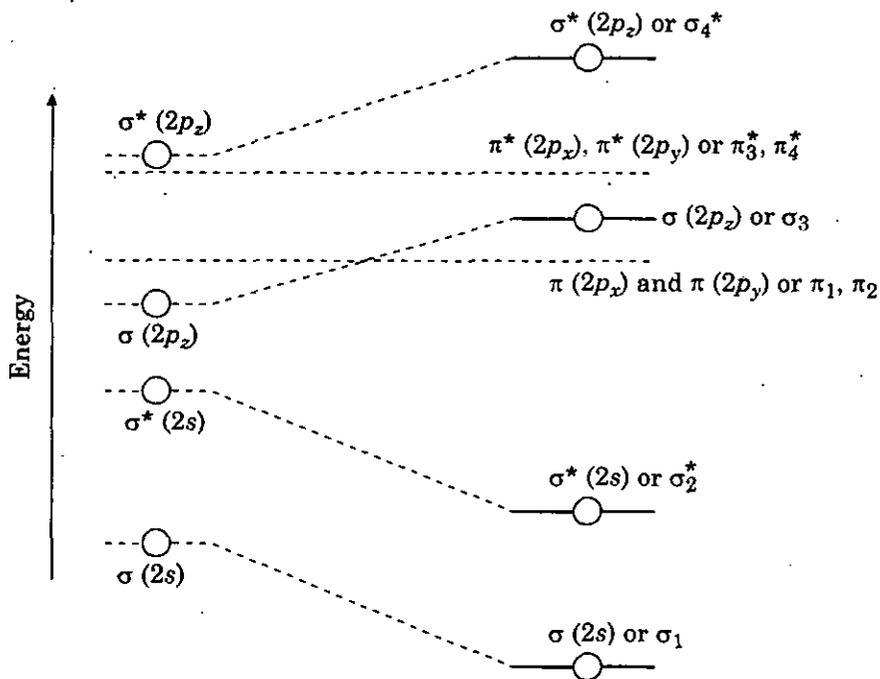
It is observed that for some elements (Li, Be, B, C and N) the above energy level is not correct. For these elements the energy level of  $\sigma(2p_z)$  MO is higher than  $\pi(2p_x)$  or  $\pi(2p_y)$  MOs. This is due to the mixing of  $2s$  and  $2p_z$  AOs as discussed here.

**Mixing of Orbitals :** We know that due to the combination of  $2s$  AOs of two atoms  $\sigma(2s)$  and  $\sigma^*(2s)$  MOs are formed. In the same way by the combination of  $2p_z$  AOs of two atoms  $\sigma(2p_z)$  and  $\sigma^*(2p_z)$  are formed. But if the difference between  $2s$  and  $2p$  AOs is smaller, then there is possibility of the mixing of  $2s$  and  $2p_z$  AOs to acquire **sp character**. Under this condition neither  $\sigma(2s)$  and  $\sigma^*(2s)$  MOs retain pure  $s$  character nor  $\sigma(2p_z)$  and  $\sigma^*(2p_z)$  MOs retain pure  $p$  character. Due to this  $sp$  mixing,



Energy level of different molecular orbitals

the energies of these four MOs change in such a way that  $\sigma(2s)$  and  $\sigma^*(2s)$  become more stable (attain lower energy level) and  $\sigma(2p_z)$  and  $\sigma^*(2p_z)$  become less stable (attain higher energy level) as shown below.



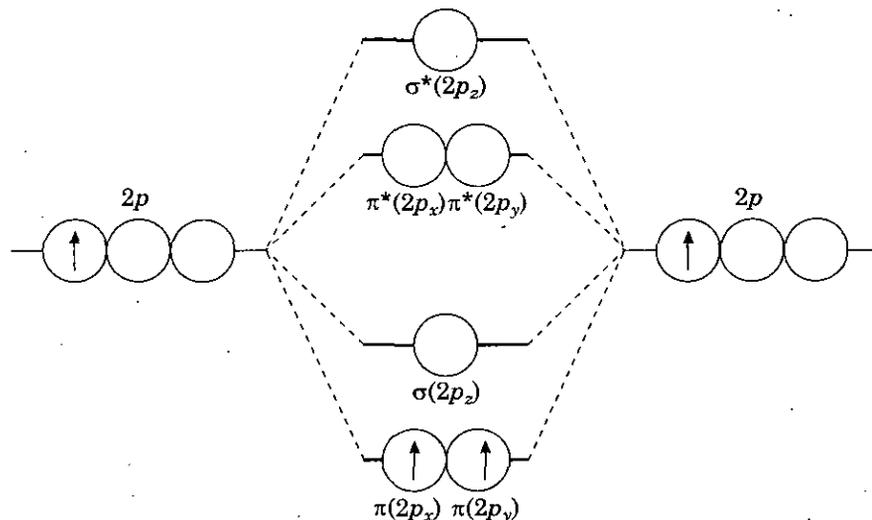
Normal energies of MOs before mixing      New energies of MOs after the mixing of  $s$  and  $p_z$  AOs

The change in energy levels of MOs during the mixing of  $s$  and  $p_z$  AOs

Because  $\pi(p)$  orbitals are not involved in mixing therefore their energy levels remain unchanged as shown in the figure. Due to this fact a new sequence of energy of  $MOs$  is obtained, which is given below :

$$\sigma(1s) < \sigma^*(1s) < \sigma(2s) < \sigma^*(2s) < \pi(2p_x) = \pi(2p_y) < \sigma(2p_z) < \pi^*(2p_x) = \pi^*(2p_y) < \sigma^*(2p_z)$$

The above energy level of different  $MOs$  is shown in the following figure :



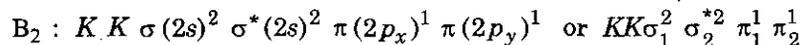
It is very important to note that the above sequence of the energy level is for Li, Be, B, C, N atoms. The reason is that the difference in energy levels between  $2s$  and  $2p_z$  AOs for these atoms is lower while that for O and F is very large as reported in the following table.

#### Energy Difference of $2s$ and $2p_z$ AOs of some Elements

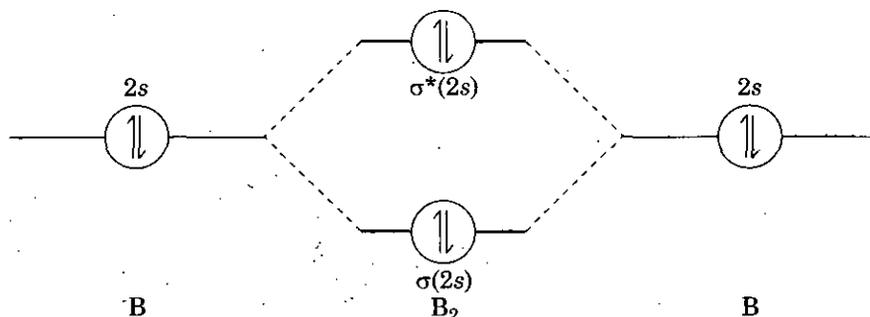
Atoms	Li	Be	B	C	N	O	F
Difference between energies of $2s$ and $2p_z$ AOs ( $\text{kJ mol}^{-1}$ )	178	262	449	510	570	1430	1970

**Molecular Orbital :** Configuration of some diatomic molecules are given here.

1. **Boron molecule ( $B_2$ ) :** The electronic configuration of boron is  $1s^2 2s^2 2p^1$ . It means there are ten electrons in  $B_2$  molecule, out of which four electrons belong to  $K$ -shells and six electrons are distributed as  $\sigma(2s)^2, \sigma^*(2s)^2, \pi(2p_x)^1$  and  $\pi(2p_y)^1$   $MOs$ . Thus the  $MO$  configuration of  $B_2$  is as :



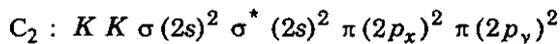
$$B.O. = \frac{1}{2} (4 - 2) = 1$$



MO energy level diagram for  $B_2$  molecule

The bond dissociation energy and bond length of B<sub>2</sub> molecule have been found to be 289 kJ mole<sup>-1</sup> and 1.59 Å respectively.

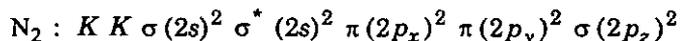
2. **Carbon molecule (C<sub>2</sub>):** The electronic configuration of carbon is 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>2</sup>. Thus there are twelve electrons in C<sub>2</sub> molecule which are distributed in different MOs as :



$$B.O. = \frac{1}{2} (6 - 2) = 2$$

Since there is no unpaired electron in C<sub>2</sub> molecule hence it is diamagnetic in nature as expected. Its bond energy and bond length have been found to be 627.9 kJ mol<sup>-1</sup> and 1.31 Å respectively.

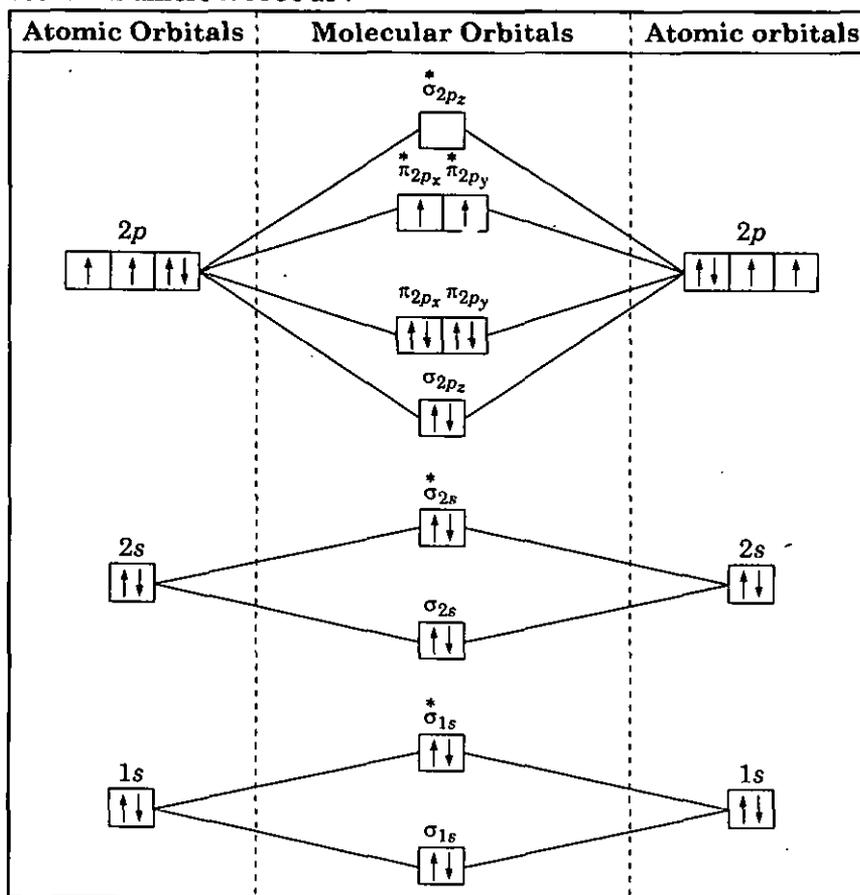
3. **Nitrogen molecule (N<sub>2</sub>):** The electronic configuration of nitrogen is 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>3</sup>. Thus there are fourteen electrons in N<sub>2</sub> molecule which are distributed in different MOs as :



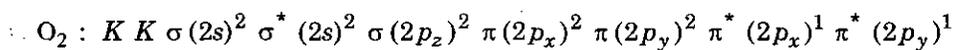
$$B.O. = \frac{1}{2} (8 - 2) = 3$$

Thus nitrogen molecule contains a triple bond. It is diamagnetic in nature as expected. Because in this case there are four bonding orbitals and only one antibonding orbital, therefore it should be a highly stable molecule. Its bond dissociation energy and bond length have been found to be 945.6 kJ mol<sup>-1</sup> and 1.10 Å respectively.

4. **Oxygen molecule (O<sub>2</sub>):** The electronic configuration of oxygen is 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>4</sup>. Thus oxygen molecule has 16 electrons out of which 12 electrons are distributed in different MOs as :



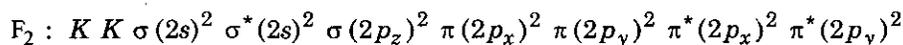
MO energy level diagram for O<sub>2</sub> molecule



$$B.O. = \frac{1}{2}(8 - 4) = 2$$

Thus oxygen molecule contains a **double bond**. It is **paramagnetic** due to the presence of two unpaired electrons. Since there are four antibonding electrons hence it is less stable (or more reactive) than nitrogen molecule. Its bond energy is  $494.6 \text{ kJ mol}^{-1}$  and bond length is  $1.21 \text{ \AA}$ .

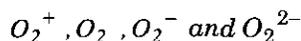
**5. Fluorine molecule ( $F_2$ ) :** The electronic configuration of fluorine is  $1s^2 2s^2 2p^5$ . Thus fluorine molecule has 18 electrons out of which 14 electrons are distributed in different *MOs* as :



$$B.O. = \frac{1}{2}(8 - 6) = 1$$

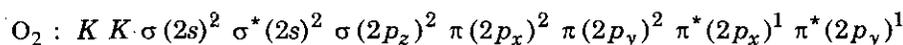
Thus a fluorine molecule contains a **single bond** and it is **diamagnetic** in nature as expected. Since there are four bonding orbitals and three antibonding orbitals hence  $F_2$  molecule is more reactive than  $O_2$  molecule. Its bond dissociation energy is  $155 \text{ kJ mol}^{-1}$  and bond length is  $1.42 \text{ \AA}$ .

**Example 4 :** Write the molecular orbital configuration of the following species :



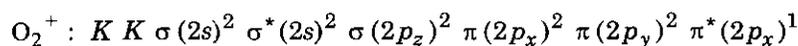
Which would have the maximum bond strength ?

**Solution :** The molecular orbital diagram for oxygen molecule ( $O_2$ ) and other species are as follows :



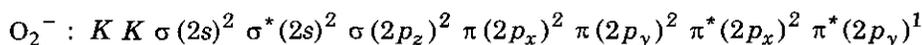
$$B.O. = \frac{1}{2}(8 - 4) = 2$$

In  $O_2^+$  species one electron is removed from  $\pi$  anti-bonding orbitals of  $O_2$  molecule [i.e.  $\pi^*(2p_x)$  or  $\pi^*(2p_y)$ ]. Thus,



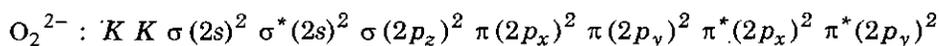
$$\therefore B.O. = \frac{1}{2}(8 - 3) = 2.5$$

In  $O_2^-$  species one electron is added in  $\pi$ -antibonding orbitals of  $O_2$  molecule. Thus,



$$\therefore B.O. = \frac{1}{2}(8 - 5) = 1.5$$

In  $O_2^{2-}$  species two electrons are added in  $\pi$ -antibonding orbitals of  $O_2$  molecule. Thus,



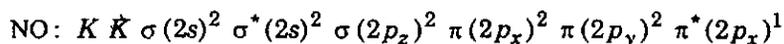
$$\therefore B.O. = \frac{1}{2}(8 - 6) = 1$$

We know that higher bond orders are associated with higher bond strength and shorter bond length. Thus  $O_2^+$  species has maximum bond strength.

Some parameters of  $O_2^+$ ,  $O_2$ ,  $O_2^-$  and  $O_2^{2-}$  are as follows :

Parameter	$O_2^+$	$O_2$	$O_2^-$	$O_2^{2-}$
Bond order	2.5	2.0	1.5	1
Bond energy ( $\text{kJ mol}^{-1}$ )	642	494	394	210
Bond length (Å)	1.12	1.21	1.25	1.49

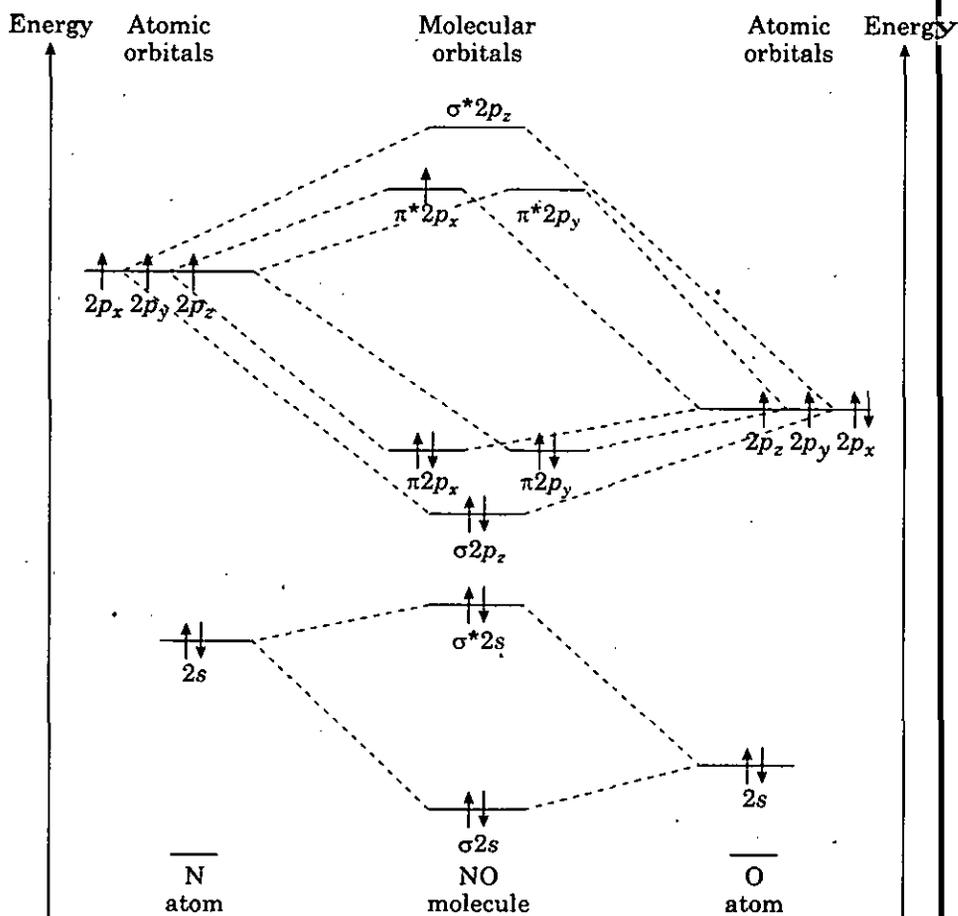
6. Nitric Oxide molecule (NO) : The electronic configuration of nitrogen and oxygen atoms is  $1s^2 2s^2 2p^3$  and  $1s^2 2s^2 2p^4$  respectively. In this case only 11 electrons are to be adjusted in different MOs. These electrons are distributed as :



$$B.O. = \frac{1}{2} (8 - 3) = 2.5$$

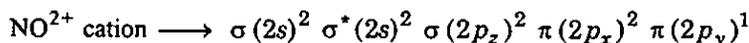
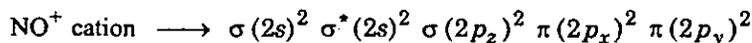
Due to the presence of one unpaired electron NO molecule is paramagnetic.

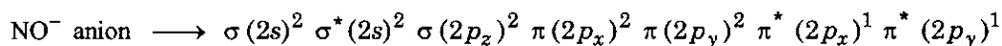
If we compare the stability of NO molecule with  $N_2$  and  $O_2$  molecules, we find that in NO molecule there is one electron extra in antibonding orbital as compared to  $N_2$  molecule therefore NO molecule is less stable (bond energy  $667.8 \text{ kJ mol}^{-1}$ ) than  $N_2$  molecule (bond energy  $945.9 \text{ kJ mol}^{-1}$ ). Similarly we can prove that NO molecule is more stable than  $O_2$  molecule (bond energy  $494.6 \text{ kJ mol}^{-1}$ ).



MO energy level diagram for NO molecule

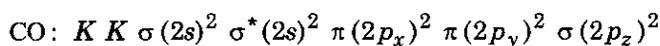
Similarly we may write the molecular configuration of  $NO^+$  (nitrosyl or nitrosium cation),  $NO^{2+}$  and  $NO^-$  ions as follows :





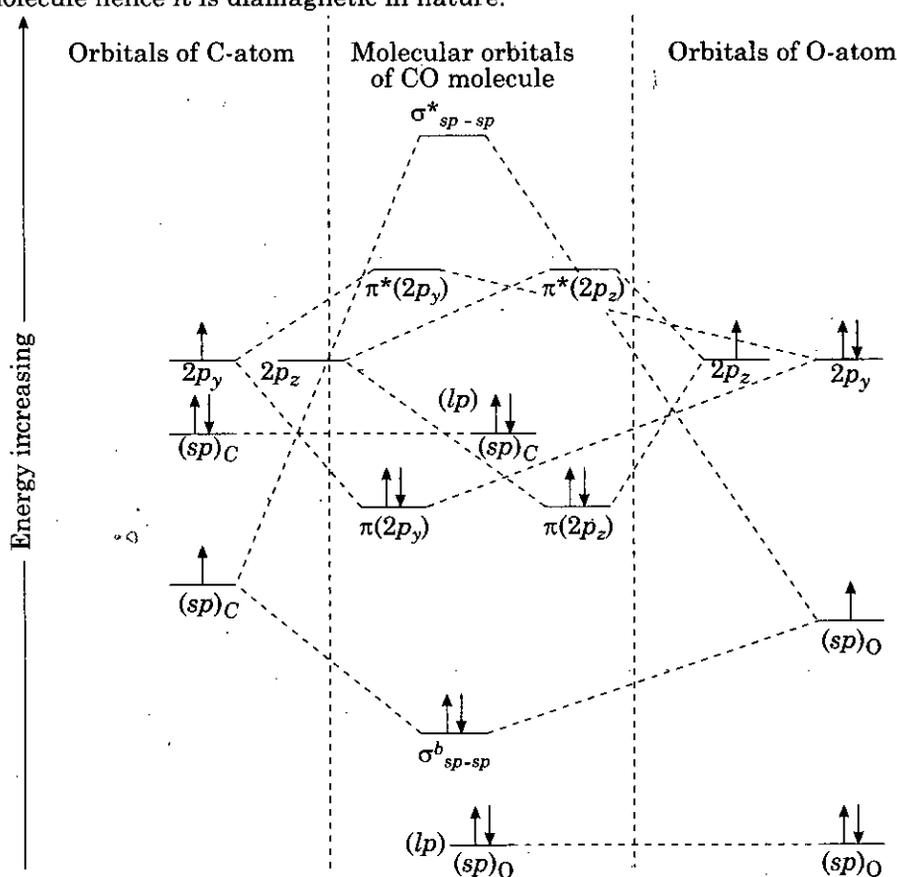
Evidently the bond order (B.O.) for  $\text{NO}^+$ ,  $\text{NO}^{2+}$  and  $\text{NO}^-$  is 3, 2.5 and 2 respectively. Since B.O. is decreasing as  $\text{NO}^+ > \text{NO}^{2+} > \text{NO}^-$ , hence bond energy decreases  $\text{NO}^+ > \text{NO}^{2+} > \text{NO}^-$  and bond length increases as  $\text{NO}^+ < \text{NO}^{2+} < \text{NO}^-$ .  $\text{NO}^+$  cation does not possess unpaired electrons hence it is **diamagnetic** while  $\text{NO}^{2+}$  and  $\text{NO}^-$  ions are **paramagnetic** due to the presence of unpaired electrons.

**7. Carbon monoxide molecule (CO) :** The electronic configuration of carbon and oxygen atoms is  $1s^2 2s^2 2p^2$  and  $1s^2 2s^2 2p^4$  respectively. In CO molecule the electrons of the K-shells do not take part in the formation of MOs. Thus four electrons ( $2s^2 2p^2$ ) and six electrons ( $2s^2 2p^4$ ) i.e. ten electrons are involved in the formation of MOs. These electrons are distributed in different MOs as follows :



$$\text{B.O.} = \frac{1}{2} (8 - 2) = 3$$

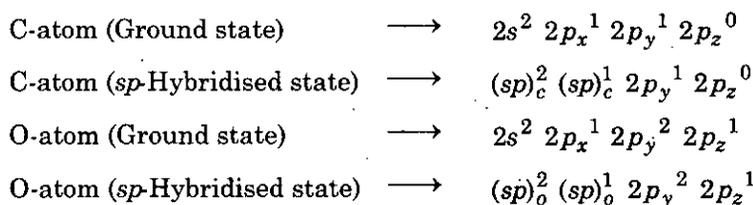
Thus CO molecule contains a **triple bond**. Its bond energy is very high ( $1067 \text{ kJ mol}^{-1}$ ) and bond length is equal to  $1.14 \text{ \AA}$ . Since there is no unpaired electron in CO molecule hence it is diamagnetic in nature.



MO energy level diagram for CO molecule as suggested by Coulson

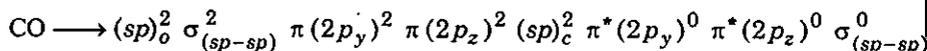
According to Coulson the MO diagram for CO given here is not correct. He suggested to adopt concept of hybridisation for CO molecule as shown in figure which is as follows:

In CO molecule both C and O-atoms undergo  $sp$ -hybridisation as below :



It is important to note that in carbon atom, fully filled  $sp$ -hybrid orbital  $[(sp)_c^2]$  has higher energy than that of half filled  $sp$ -hybrid orbital  $[(sp)_c^1]$ . This order is reversed in oxygen atom i.e.  $[(sp)_o^2]$  has lower energy than that of  $[(sp)_o^1]$  hybrid orbital. As usual  $p_y$  and  $p_z$  orbitals of both carbon and oxygen atoms have same energy. In both these atoms lone pairs residing in  $sp$  hybrid orbitals remain as lone pair ( $lp$ ) of electron and do not participate in the formation of CO molecule. Therefore these pairs of electrons are known as *non-bonding electron pairs*.

Now half filled  $sp$ -hybrid orbitals of both C and O atoms overlap to form  $\sigma_{(sp-sp)}$  MO which has two bonding electrons. Its energy is lower than that of both  $sp$ -hybrid orbitals of C and O atoms. While  $\sigma_{sp-sp}^*$  MO has a very large energy. The  $p_y$  and  $p_z$  orbitals of C and O atoms overlap as usual to form four MOs such as  $\pi(2p_y)^2$ ,  $\pi(2p_z)^2$ ,  $\pi^*(2p_y)^0$  and  $\pi^*(2p_z)^0$ . These orbitals are perpendicular to molecular axis i.e.  $x$ -axis. Thus the molecular configuration of CO may be given as :

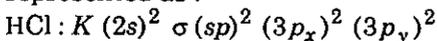


As expected bond order, in this case, is also 3 having one  $\sigma$  and two  $\pi$  bonds.

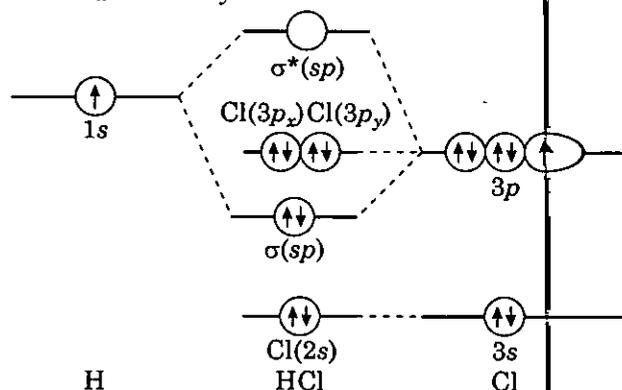
**8. Hydrogen chloride molecule (HCl) :** The electronic configuration of hydrogen and chlorine is  $1s^1$  and  $1s^2 2s^2 2p^6 3s^2 3p^5$  respectively. Hence there is one unpaired electron each in hydrogen atom and chlorine atom which can combine effectively along the axis. In this way  $\sigma(sp)$  MO is formed.

Thus in the formation of HCl molecule  $3s^2$ ,  $3p_x^2$  and  $3p_y^2$  electrons of chlorine do not take part in the formation of MOs.

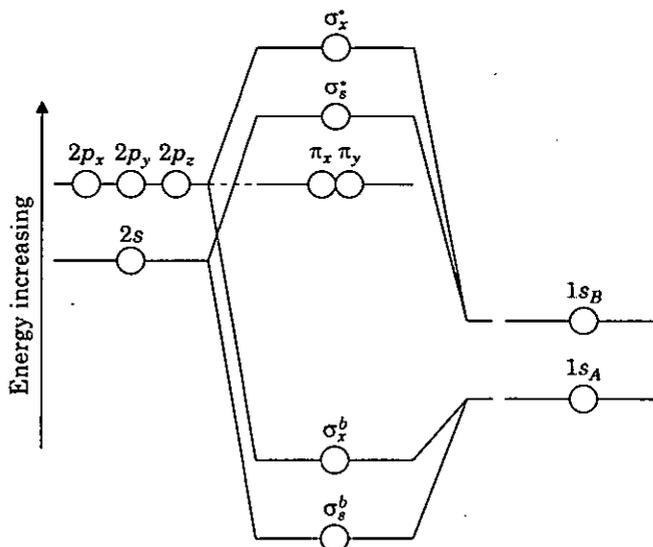
Only  $1s^1$  electron of hydrogen atom and  $3p_z^1$  electron of chlorine atom combine to form  $\sigma(sp)$  MO which contains two electrons. The energy level of  $\sigma(sp)$  MO is lower than  $3p_x$  and  $3p_y$  AOs. Hence the MO configuration of HCl molecule may be represented as :



The MO diagram for HCl molecule is given in the figure.



**9. Beryllium Hydride ( $BeH_2$ ) :** It is a linear molecule (similar to  $BeF_2$ ). When  $2s$  and  $2p_x$  orbitals of Be and  $1s$  orbitals of H-atoms overlap MOs for  $BeH_2$  are formed. Its M.O. configuration may be written as



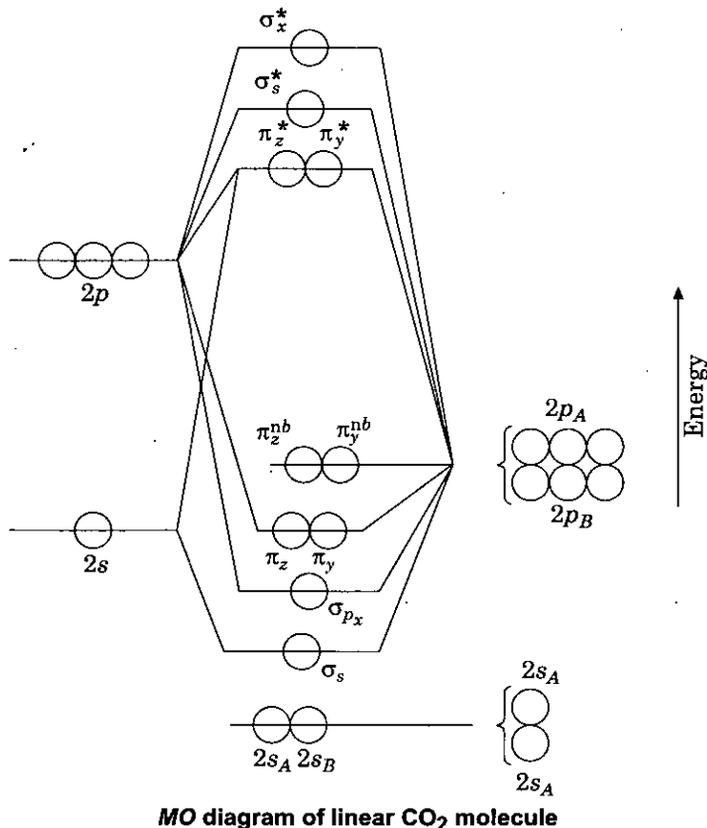
MO diagram for  $BeH_2$  molecule

$$\sigma(s^2) \sigma(2p_x)^2$$

The molecular orbital diagram of  $\text{BeH}_2$  may be represented as above.

**10. Carbon dioxide ( $\text{CO}_2$ ):** It is a linear molecule. Let molecular axis be  $x$ -axis. Therefore  $2p_y$  and  $2p_z$  orbitals form  $\pi$ -bonds. In this case six  $\pi$ -molecular orbitals are generated which are perpendicular to  $x$ -axis. Two each of them are bonding, non-bonding and antibonding.

The energy level diagram for  $\text{CO}_2$  may be given as follows :



There are 16 valence electrons to be filled in these MOs. Out of these, eight electrons are filled in four non-bonding MOs [ $2s_A$ ,  $2s_B$ ,  $\pi^{nb}(2p_y)$  and  $\pi^{nb}(2p_z)$ ] and eight electrons are filled in four bonding MOs [ $\sigma(2s)$ ,  $\sigma(2p_x)$ ,  $\pi(2p_y)$  and  $\pi(2p_z)$ ]. Thus in  $\text{CO}_2$  molecule there are two  $\sigma$  bonds and two  $\pi$  bonds, or there are two double bonds in  $\text{CO}_2$  molecule ( $\text{O}=\text{C}=\text{O}$ ). It is also noted that the filled orbitals are more stable when the molecule is linear, therefore it is concluded that  $\text{CO}_2$  molecule is a linear molecule.

### Comparison of VBT and MOT

#### Similarities between VBT and MOT :

- (i) They account for the directional nature of the bond.
- (ii) Bond results by the overlapping of two orbitals of minimum energy.
- (iii) Electronic charge persists in between two atomic nuclei in bond formation.
- (iv) Atomic orbitals should be of same energy overlap and have same symmetry.

#### Dis-similarities between VBT and MOT

	VBT	MOT
1.	Interatomic orbitals are produced by multiplying, exchanging and combinations of space wave functions of two unpaired electrons.	Molecular orbitals are formed by LCAO of all atomic orbitals from the valency shell of two atoms.

2.	Orbitals of bonded atoms cannot lose their identity.	Orbitals of bonded atoms lose their individual identity.
3.	Atomic orbitals are monocentric.	Molecular orbitals are polycentric.
4.	It explains that inert gases have orbital already spin paired, so they have no tendency to form any linkage.	Molecular orbitals theory fails to explain the existence of molecular state of inert gases, since number of bonding and antibonding electrons are equal.
5.	Pauli's exclusion principle decides the spin function combination with wave functions as $\uparrow\downarrow$ Bonding $\uparrow\uparrow$ Antibonding	It explains how electrons are originally present in atomic orbitals and are distributed in new molecular orbitals.
6.	VBT introduces a special form to explain the presence of ionic character in bond.	MOT is capable of predicting ionic character in a bond.

**Formal Charge :** It is the charge that an atom in a molecule would have if all the atoms had the almost same electronegativity. It may be calculated by the following formula :

$$Q_f = N_A - N_{lp} - \frac{1}{2}N_{bp}$$

where  $Q_f$  = Formal charge

$N_A$  = No. of electrons in the valence shell in free atom.

$N_{lp}$  = No. of electrons in lone pairs (unshared pairs)

$N_{bp}$  = No. of electrons in bonding pairs

**Examples : 1.  $H_2O$  :** The Lewis structure of  $H_2O$  may be given as  $H-\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}-H$

$$\begin{aligned} \text{For 'O'} \quad Q_f &= N_A - N_{lp} - \frac{1}{2}N_{bp} \\ &= 6 - 2 \times 2 - \frac{1}{2} \times 2 \times 2 = 6 - 4 - 2 = 0 \end{aligned}$$

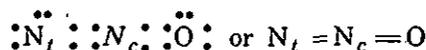
$$\begin{aligned} \text{For 'H'} \quad Q_f &= N_A - N_{lp} - \frac{1}{2}N_{bp} \\ &= 1 - 0 \times 2 - \frac{1}{2} \times 2 = 1 - 0 - 1 = 0 \end{aligned}$$

**2.  $H_3O^+$  :** The Lewis structure of  $H_3O^+$  may be given as  $H-\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}-H$   
 $\quad \quad \quad |$   
 $\quad \quad \quad H$

$$\begin{aligned} \text{For 'O'} \quad Q_f &= N_A - N_{lp} - \frac{1}{2}N_{bp} \\ &= 6 - 1 \times 2 - \frac{1}{2} \times 2 \times 3 = 6 - 2 - 3 = +1 \end{aligned}$$

$$\begin{aligned} \text{For 'H'} \quad Q_f &= N_A - N_{lp} - \frac{1}{2}N_{bp} \\ &= 1 - 0 \times 2 - \frac{1}{2} \times 2 \times 3 = 1 - 0 - 1 = 0 \end{aligned}$$

**3.  $N_2O$  :** The Lewis structure of  $N_2O$  may be given as



$$\text{Since, } Q_f = N_A - N_{lp} - \frac{1}{2}N_{bp}$$

$$\text{For 'N}_t\text{' } Q_f = 5 - 2 \times 2 - \frac{1}{2} \times 2 \times 2 = 5 - 4 - 2 = -1$$

$$'N_c' Q_f = 5 - 0 \times 2 - \frac{1}{2} \times 2 \times 4 = 5 - 0 - 4 = +1$$

$$'O' Q_f = 6 - 2 \times 2 - \frac{1}{2} \times 2 \times 2 = 6 - 4 - 2 = 0$$

4. CO : The Lewis structure of CO may be given as  $:\ddot{C}::\ddot{O}:$

$$\text{Since } Q_f = N_A - N_{lp} - \frac{1}{2} N_{bp}$$

$$\text{For 'C' } Q_f = 4 - 1 \times 2 - \frac{1}{2} \times 2 \times 3 = 4 - 2 - 3 = -1$$

$$'O' Q_f = 6 - 1 \times 2 - \frac{1}{2} \times 2 \times 3 = 6 - 2 - 3 = +1$$

5. SO<sub>3</sub> : The Lewis structure of SO<sub>3</sub> may be given as  $:\ddot{O}::\ddot{S}::\ddot{O}:$



$$\text{Since } Q_f = N_A - N_{lp} - \frac{1}{2} N_{bp}$$

$$\text{Since 'S' } Q_f = 6 - 0 \times 2 - \frac{1}{2} \times 2 \times 6 = 6 - 0 - 6 = 0$$

$$'O' Q_f = 6 - 2 \times 2 - \frac{1}{2} \times 2 \times 2 = 6 - 4 - 2 = 0$$

### • 2.13. VALENCE SHELL ELECTRON PAIR REPULSION (VSEPR) THEORY

This theory was proposed by R.J. Gillespie and R.S. Nyholm in 1957 and was given to account for the geometry of covalent molecules. The main points of this theory are :

(i) The geometry of the covalent molecules depends upon the number of shared and lone pairs of electrons around central atom of the molecule. These electron pairs are arranged in space as apart as possible so that there is a minimum repulsion and maximum stability.

(ii) The molecule will have regular geometry if all the hybrid orbitals of central atom contain only shared pairs of electrons.

(iii) The geometry of the molecule is distorted if one or more hybrid orbitals of central atom contain lone pair of electrons. The presence of lone pairs decreases the bond angle because the repulsion between the two lone pairs is greater than the repulsion between lone pair and bond pair of electrons which, in turn, is greater than repulsion between two bond pairs of electrons.

lone pair-lone pair repulsion > lone pair-bond pair repulsion > bond pair-bond pair repulsion

(iv) Greater is the number of lone pairs of electrons on the central atom, greater will be the distortion in the geometry of the molecule.

(v) The lesser is the electronegativity of the central atom (the number of electron pairs surrounding central atom and nature of the attached atoms being the same), the larger is the bond angle.

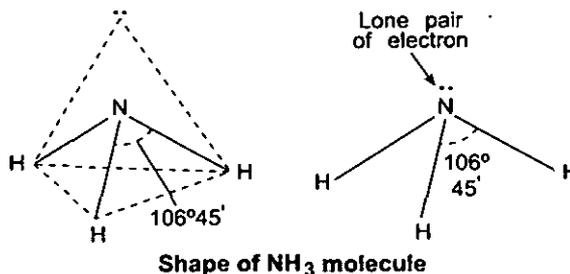
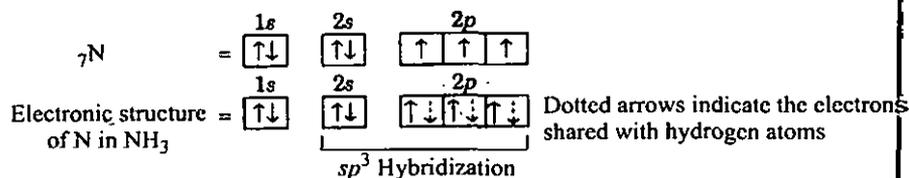
For example,

NH <sub>3</sub>	PH <sub>3</sub>	AsH <sub>3</sub>
106° 45'	93° 20'	91° 50'

Nitrogen atom is sp<sup>3</sup> hybridized,

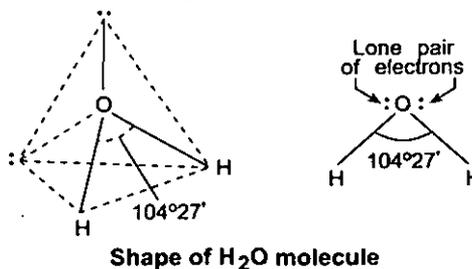
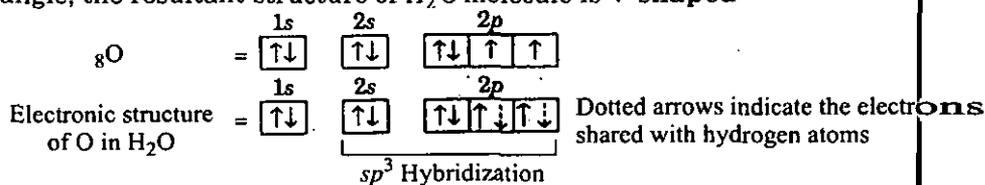
(i) NH<sub>3</sub> : In the case of NH<sub>3</sub>, three of the hybrid orbitals are used for bond formation and contain shared pairs of electrons, whereas the fourth hybrid orbital contains a lone pair of electrons. The bond angle in this case is reduced from 109° 28' to 106° 45' because the repulsion between the lone pair and shared pair is greater than that between the

two shared pairs. Due to this distortion in the bond angle, the resulting structure of  $\text{NH}_3$  is pyramidal.

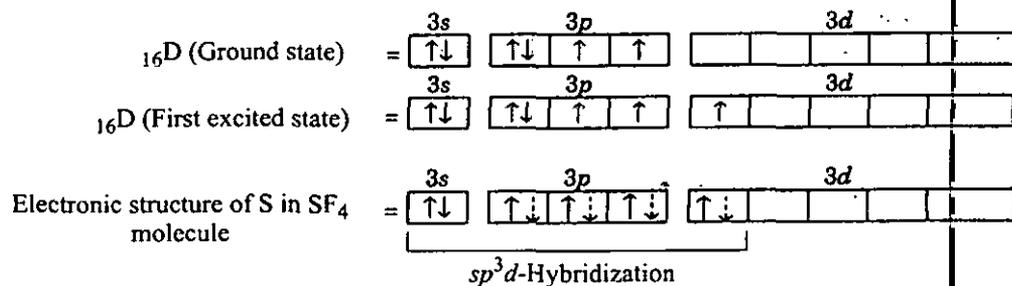


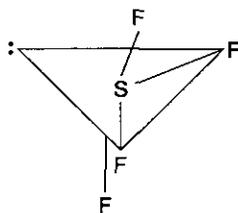
(2)  $\text{H}_3\text{O}^+$  : In this ion, oxygen atom is  $\text{sp}^3$  hybridized. Two hybrid orbitals containing one electron each form bond with two H-atoms and contain shared pairs of electrons whereas one hybrid orbital containing a lone pair of electron forms bond with  $\text{H}^+$  ion. The fourth hybrid orbital containing a lone pair of electron remains unused. The resulting shape of the molecule is pyramidal just like  $\text{NH}_3$ .

(3)  $\text{H}_2\text{O}$  : In the case of  $\text{H}_2\text{O}$ , only two hybrid orbitals are used for bond formation and contain shared pairs of electrons whereas rest two hybrid orbitals contain lone pairs of electrons. The bond angle in this case is further reduced to  $104^\circ 27'$  because the two lone pairs of electrons repel each other more strongly and cause the two O—H bonds to come closer to each other than in the case of  $\text{NH}_3$ . Due to this distortion in the bond angle, the resultant structure of  $\text{H}_2\text{O}$  molecule is V-shaped



(4)  $\text{SF}_4$  : In  $\text{SF}_4$ , sulphur atom undergoes  $\text{sp}^3d$  hybridization. In this molecule, four hybrid orbitals are used for bond formation and contain shared pair of electrons whereas one hybrid orbital contains lone pair of electrons, as shown below :

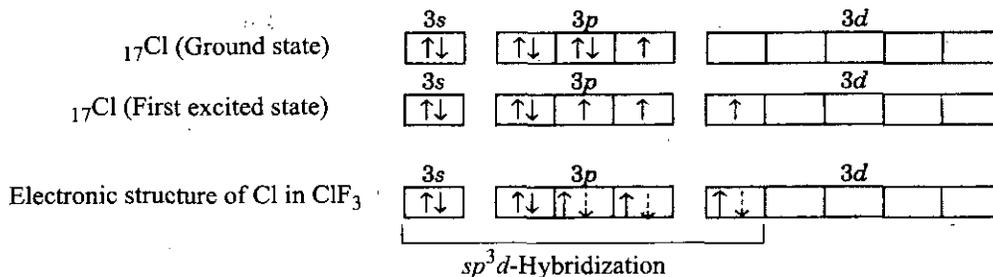




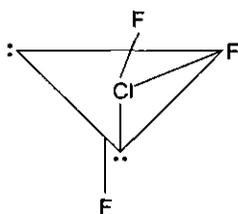
Structure of SF<sub>4</sub>

The molecule should have trigonal bipyramidal structure but its shape is distorted (*i.e.*, see saw) due to the presence of lone pair of electrons.

(5) ClF<sub>3</sub> : In ClF<sub>3</sub>, chlorine atom undergoes  $sp^3d$  hybridization. In this molecule, three hybrid orbitals are used for bond formation and contain shared pair of electrons whereas rest two hybrid orbitals contain lone pair of electrons as shown below :

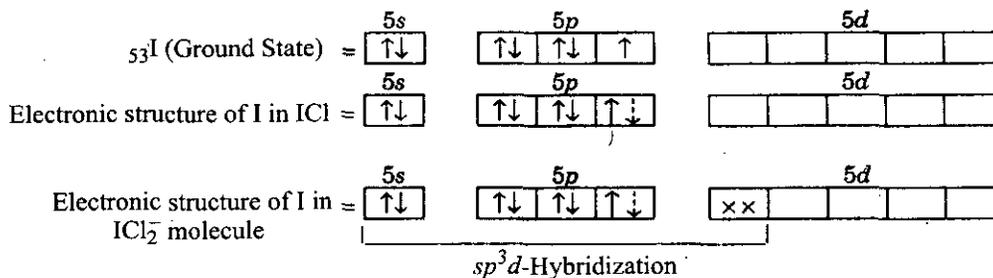


This gives the molecule a trigonal bipyramidal structure but due to the presence of two lone pairs of electrons, the shape of the molecule is distorted and becomes slightly T-shaped with bond angle 87.5°.

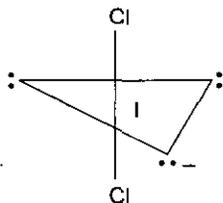


Structure of ClF<sub>3</sub>

(6) ICl<sub>2</sub><sup>-</sup> : In ICl<sub>2</sub><sup>-</sup>, iodine atom undergoes  $sp^3d$  hybridization as shown :



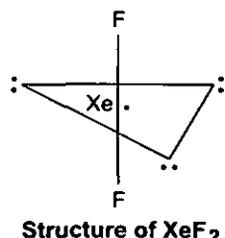
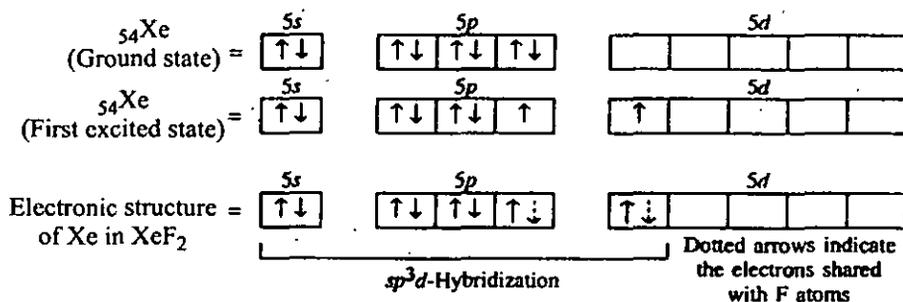
(Cross indicate the lone pair of electrons donated by Cl<sup>-</sup> ions).



Structure of ICl<sub>2</sub><sup>-</sup>

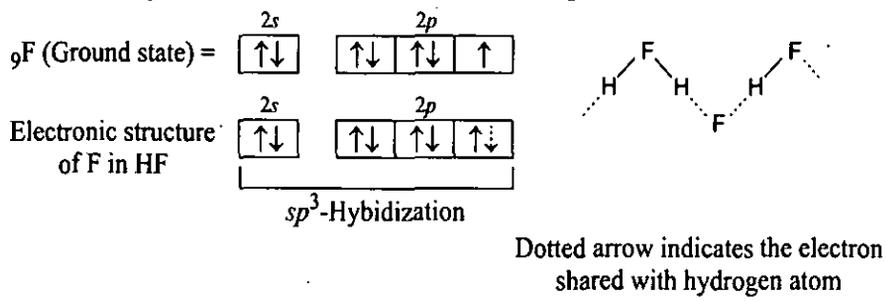
This gives the molecule a trigonal bipyramidal structure but due to the presence of three lone pairs of electrons, the shape of the molecule is distorted and the molecule assumes a linear structure.

(7) In  $\text{XeF}_2$ , Xe atom involves  $sp^3d$  hybridization as shown below :



Thus, in  $\text{XeF}_2$  molecule, Xe atom contains five completely filled hybrid orbitals, two of which contain shared pair of electrons and the remaining three contain lone pairs of electrons. This gives the molecule a trigonal bipyramidal structure but due to the presence of three lone pair of electrons, the shape of the molecule is distorted and the molecule assumes a linear structure.

(8)  $\text{H}-\text{F}$  : In HF, fluorine atom undergoes  $sp^3$  hybridization. In this molecule, one hybrid orbital is used for bond formation and contains shared pair of electrons, whereas remaining three hybrid orbitals contain lone pair of electrons as shown below:



This gives the molecule a tetrahedral structure but due to the presence of three lone pair of electrons, the shape of the molecule is distorted and becomes linear.

**Limitations :**

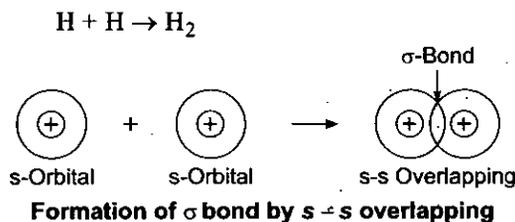
- (i) The theory is applicable to covalent compounds only. It can not be applied to ionic compounds.
- (ii) The theory does not make any distinction between the electrons present in  $s$ ,  $p$ , and  $f$ -orbitals of the same valency shell.
- (iii) The theory fails to predict the exact bond angles in the molecules like  $\text{NH}_3$  and  $\text{H}_2\text{O}$  which do not have regular geometries.
- (iv) The theory does not explain the shapes of coordination compounds.
- (v) The theory does not explain the difference in the bond angles in a series of compounds, such as  $\text{NH}_3$ ,  $\text{PH}_3$ ,  $\text{AsH}_3$  etc. in which different central atom is bonded to similar atoms.

**• 2.14. MULTIPLE BONDING ( $\sigma$  AND  $\pi$  BOND)**

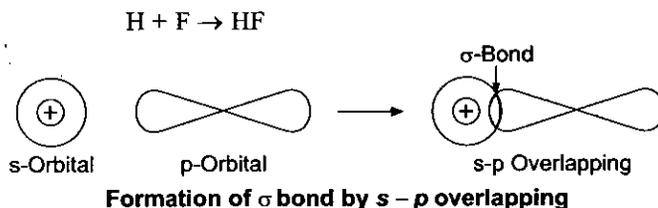
According to orbital concept a covalent bond is formed by the overlapping of atomic orbitals. This overlapping can take place either along the axes of orbitals or perpendicular to their axes. Thus, it gives rise to two types of bonds,  $\sigma$ - and  $\pi$ -bonds.

**(1) Sigma ( $\sigma$ ) bond :** The bond formed as a result of coaxial (or end to end) overlapping of atomic orbitals is known as  $\sigma$ -bond. Such a bond results from the overlapping of  $s-s$ ,  $s-p$  or  $p-p$  orbitals along their axes. This bond is a strong bond as the overlapping is maximum.

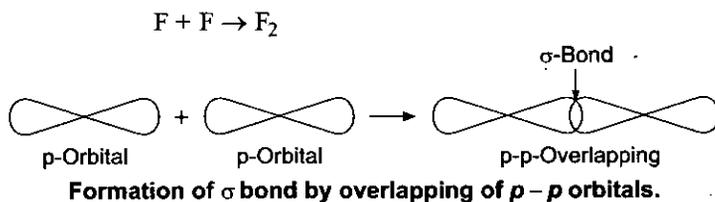
**$s-s$  overlapping :** Since the  $s$ -orbital is spherically symmetrical, its overlapping with other  $s$ -orbital will always be maximum and will result in the formation of a  $\sigma$ -bond. For example :



**$s-p$  overlapping :** Formation of  $\sigma$ -bond as a result of  $s-p$  overlapping is illustrated by the formation of halogen acids (HF, HCl etc.).

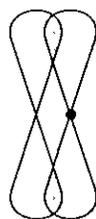
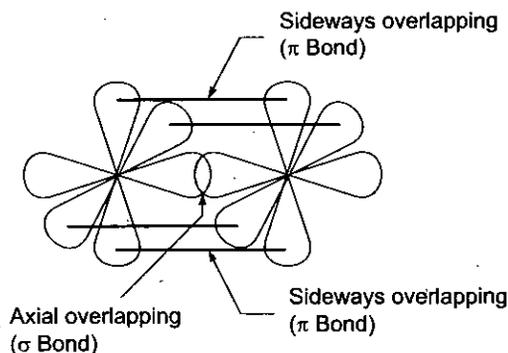


**$p-p$  overlapping :** Formation of  $\sigma$ -bond as a result of axial overlapping of  $p-p$  orbitals is illustrated by the formation of halogen molecules ( $F_2$ ,  $Cl_2$  etc.).



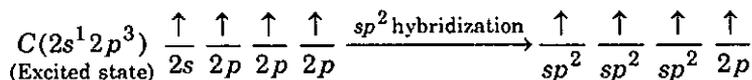
**(2) Pi ( $\pi$ ) bond :** The bond formed as a result of sideways overlapping of  $p-p$  orbitals is known as  $\pi$ -bond. In this case, the overlapping is only partial and, therefore, the bond formed is weak. The  $\pi$ -bond is formed when  $\sigma$ -bond is already present in the molecule.

**Formation of a  $N_2$  molecule.** The electronic configuration of nitrogen is  $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$ . Thus, nitrogen has three half filled  $p$ -orbitals. In the formation of nitrogen molecule, these three half filled orbitals of one nitrogen atom can overlap with those of the other nitrogen atom to form three bonds. Out of these three bonds, one bond is  $\sigma$ , whereas the rest two are a  $\pi$  as shown in figure.

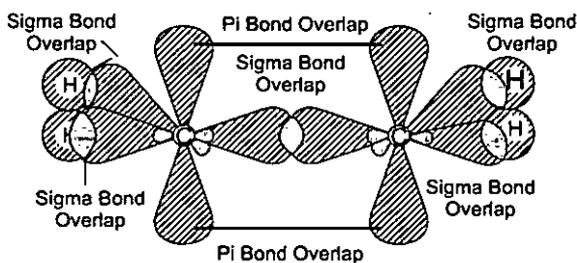


**Sideways overlapping of  $p-p$  orbitals**

**Formation of C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>2</sub> molecules :** In C<sub>2</sub>H<sub>4</sub> molecule, carbon undergoes  $sp^2$ -hybridization as :

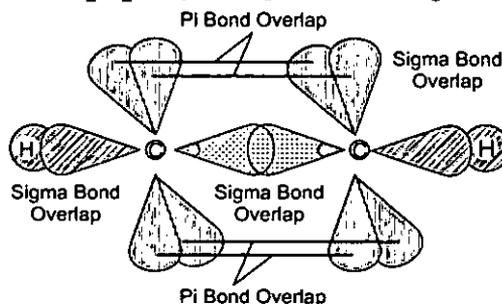


In this way there are four unpaired electrons out of them three belong to  $sp^2$ -hybrid orbital and one belongs to  $2p$ -orbital. Similarly second carbon atom is hybridized. No one  $sp^2$ -hybrid orbital of each carbon atom overlaps to form ( $\sigma$ -bond) C—C bond. The remaining two  $sp^2$ -hybrid orbitals of one carbon atom overlap ( $\sigma$ -bond) with the  $1s$ -orbitals of two hydrogen atoms, similarly second carbon behaves. Now  $2p$ -orbitals both the carbon atoms overlaps to form  $\pi$ -bond. Hence C<sub>2</sub>H<sub>4</sub> may be represented as given in figure.



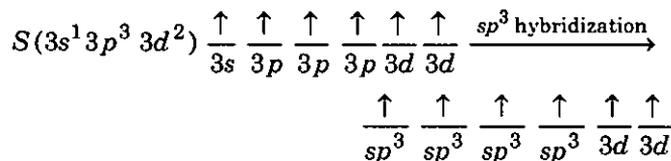
Formation of ethene molecule, C<sub>2</sub>H<sub>4</sub>

In C<sub>2</sub>H<sub>2</sub>, both the carbon atoms undergo  $sp$ -hybridization. In this way there are two  $sp$ -hybrid orbitals and two  $2p$ -orbitals all are half filled. The overlapping takes place as above to form HC≡CH in which there is one  $\sigma$ -bond and two  $\pi$ -bonds between carbon-carbon atoms. Hence C<sub>2</sub>H<sub>2</sub> may be represented as given in Figure.

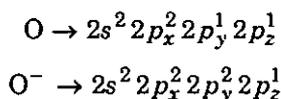


Formation of ethyne molecule, C<sub>2</sub>H<sub>2</sub>

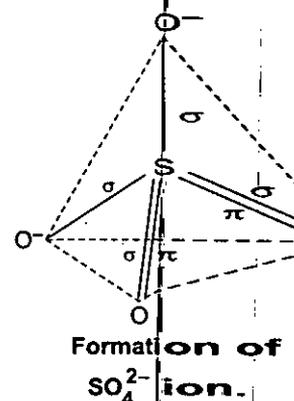
**Formation of SO<sub>4</sub><sup>2-</sup> Ion :** In SO<sub>4</sub><sup>2-</sup> ion, sulphur atom comes in second excited state thus it has six unpaired electrons (as shown in SF<sub>6</sub>) and then undergoes  $sp^3$ -hybridization as :



while oxygen atom (O) and oxygen ion (O<sup>-</sup>) have the following electronic configuration :



Now all the four half filled  $sp^3$  hybrid orbitals overlap with two  $2p$ -orbitals of oxygen atom (O) and two  $2p$ -orbitals of oxygen anion (O<sup>-</sup>) and form 4  $\sigma$ -bonds ( $sp^3$  bonds). After that two  $3d$ -orbitals overlap with two  $2p$ -orbitals of oxygen atom to form two  $\pi$ -bonds ( $d\pi-p\pi$  bonds) as shown in figure.



Formation of SO<sub>4</sub><sup>2-</sup> ion.

Differences Between  $\sigma$  and  $\pi$  Bonds

S. No.	$\sigma$ -Bond	$\pi$ -Bond
1.	The bond is formed by the coaxial or end to end overlapping of $s-s$ , $s-p$ and $p-p$ atomic orbitals.	The bond is formed by the sideways or partial overlapping of $p-p$ atomic orbitals.
2.	It is a strong bond as the atomic orbitals overlap to a considerable extent.	It is a weak bond as the atomic orbitals overlap to a little extent.
3.	It is less reactive.	It is more reactive.
4.	There can be only one $\sigma$ -bond between two atoms.	There can be more than one $\pi$ -bond between two atoms.
5.	The electron cloud of $\sigma$ -bond is symmetrical about the molecular axis.	The electron cloud of $\pi$ -bond is unsymmetrical.
6.	The free rotation of atoms about $\sigma$ -bond is possible.	The free rotation of atoms about $\pi$ -bond is not possible.
7.	The bond is formed independently <i>i.e.</i> , the bond formed without having a $\pi$ -bond in the molecule.	The bond is formed only after $\sigma$ -bond has been formed.
8.	The shape of the molecule is determined by these bonds.	The shape of the molecule is not affected by these bonds.

## • 2.15. BOND LENGTH

Since atoms in a molecule are always vibrating with respect to each other hence the question of any fixed distance between the nuclei of the atom does not arise. Even then *the average distance between the two nuclei of two bonded atoms is called bond length.*

**Determination of bond length :** There are many methods; such as X-ray method, neutron diffraction method, electron diffraction method, molecular spectral method, electronegativity method etc. to determine the bond length.

If covalent radius of an atom  $A$  is  $r_A$ , the bond length  $d_{A-A}$  of  $A-A$  bond in  $A_2$  molecule may be given as :

$$d_{A-A} = 2r_A$$

If covalent radius of an atom  $B$  is  $r_B$ , the bond length  $d_{B-B}$  of  $B-B$  bond in  $B_2$  molecule may be given as :

$$d_{B-B} = 2r_B$$

For a molecule  $AB$ ;

If the electronegativity difference ( $X_A - X_B$ ) is very small, then the bond length  $d_{A-B}$  is equal to the sum of covalent radii of atoms  $A$  and  $B$  *i.e.*,

$$d_{A-B} = r_A + r_B$$

If the electronegativity difference ( $X_A - X_B$ ) is appreciably large, then the bond length  $d_{A-B}$  may be given according to Schomaker and Stevenson equation *i.e.*,

$$d_{A-B} = r_A + r_B - 0.09(X_A - X_B)$$

Here  $r_A$  and  $r_B$  are given in  $\text{\AA}$ .

For ionic compounds it may be given as :

$$d_{A^+-B^-} = r_{A^+} + r_{B^-}$$

The bond lengths of some common diatomic molecules are given in the Table.

Bond lengths ( $\text{\AA}$ ) of Some Common Covalent Bonds

Bond	Bond length						
H—H	0.751	H—F	0.926	C—C	1.543	C—F	1.42
F—F	1.435	H—Cl	1.284	C=C	1.330	C—Cl	1.77

Bond	Bond length	Bond	Bond length	Bond	Bond length	Bond	Bond length
Cl—Cl	2.002	H—Br	1.423	C≡C	1.200	C—Br	1.91
Br—Br	2.286	H—I	1.615	O—O	1.480	C—I	2.13
I—I	2.666	H—O	0.957	O=O	1.207	C—N	1.47
N—N	1.470	H—S	1.334	C—O	1.420	C=N	1.28
N≡N	1.094	H—N	1.014	C=O	1.220	C≡N	1.15

### Factors Affecting Bond Length

It should be noted that the value given in the above table do not hold good for compounds. Because bond length is not a simply addition of the ionic or covalent radii of the two concerned atoms. There are several factors which are responsible for bond length such as :

(i) **Electronegativity** : According to Schomaker and Stevenson equation, the difference in electronegativity of elements A and B i.e.,  $(X_A - X_B)$  increases, bond length decreases.

(ii) **Bond order** : It is clear from the above table as bond order increases, bond length decreases. This is due to the fact that as the number of bonds increases between two atoms the degree of overlapping of orbitals increases and atoms come close to each other. Therefore,

$$\text{Bond order} \propto \frac{1}{\text{Bond length}}$$

(iii) **Hybridization** : Bond length decreases with the increase in the percentage s-character in a hybrid orbital.

This statement is justified by considering example  $C_2H_6$ ,  $C_2H_4$  and  $C_2H_2$  in the following table.

Molecule	Types of hybridization	% of s-character in hybridization	C—H Bond length (Å)	C—C Bond length (Å)
Ethane $H_3C-CH_3$	$sp^3$	25	1.093	1.54
Ethene $H_2C=CH_2$	$sp^2$	33.3	1.087	1.32
Ethyne $HC\equiv CH$	$sp$	50	1.057	1.20

(iv) **Resonance** : Bond length is also effected by resonance. For example, carbon-carbon bond length in  $C_6H_6$  molecule is 1.39 Å which is intermediate between the values for C—C (1.543 Å) and C=C (1.33 Å).

### • 2.16. COVALENT CHARACTER IN IONIC COMPOUNDS

There are very few molecules which are 100% ionic or 100% covalent. Thus most of the compounds possess both ionic and covalent character. The phenomenon due to which bond possesses both ionic and covalent character is known as polarisation of ions. When oppositely charged ions approach each other closely, then the cation attracts the outermost electron charged cloud and repels the nucleus of the anion and vice versa. Therefore the electron charge cloud of the anion no longer remains spherical but get distorted or deformed i.e., polarised towards the cation. The electron charge cloud of cation is also distorted but the polarisation of cation is far less polarised due to its small size. Due to polarisation electron charge cloud is concentrated between the nuclei of both the ions. Thus the bond is intermediate between an ionic and a covalent bond. Such type of the bond is known as polar covalent bond. This bond is more stable than pure covalent bond. As the degree of polarisation increases the stability of the polar covalent bond increases. Evidently the degree of polarisation depends upon

the polarising power of the cation and polarisability of the anion. The factors governing the distortion or polarisation of anion was given first of all by Fajan and is generally known as Fajan's rules.



Transition between ionic and covalent bonding.

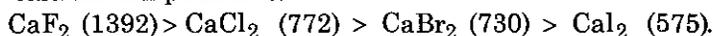
According to Fajan's rules, The increases in the degree of polarization of anion is favoured by :

(i) **Large charge on the ions (cation and anion)** : For appreciable distortion cation  $\text{Na}^+ < \text{Mg}^{2+} < \text{Al}^{3+}$  and anion should have a large charge,  $\text{F}^- < \text{O}^{2-}$ .

(ii) **Small cation and large anion** : Smaller the cation greater is the electrostatic force with which its nucleus will attract electrons of the anion, larger the anion, less strongly it can hold its outermost electrons.

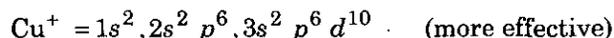
For example, the polarizing power of bivalent cations of 2nd group elements is in the order :  $\text{Be}^{2+} > \text{Mg}^{2+} > \text{Ca}^{2+} > \text{Sr}^{2+} > \text{Ba}^{2+} > \text{Ra}^{2+}$  while their ionic radii ( $\text{\AA}$ ) is in the order  $\text{Be}^{2+} (0.31) < \text{Mg}^{2+} (0.65) < \text{Ca}^{2+} (0.99) < \text{Sr}^{2+} (1.13) < \text{Ba}^{2+} (1.35) < \text{Ra}^{2+} (1.40)$ . It means maximum covalent character is with beryllium compounds which is further supported by the melting points ( $^{\circ}\text{C}$ ) of their chlorides as  $\text{BeCl}_2 (405) < \text{MgCl}_2 (712) < \text{CaCl}_2 (772) < \text{SrCl}_2 (872) < \text{BaCl}_2 (960)$ .

In the same way polarizability tendency power of monovalent anion of 17<sup>th</sup> group elements is in the order :  $\text{F}^- < \text{Cl}^- < \text{Br}^- < \text{I}^-$ . While their ionic radii ( $\text{\AA}$ ) is in the order :  $\text{F}^- (0.72) < \text{Cl}^- (0.99) < \text{Br}^- (1.14) < \text{I}^- (1.33)$ . This is supported by the melting point ( $^{\circ}\text{C}$ ) of their calcium compounds as :



(iii) **Nature of the solvent** : Solvent like water (high dielectric constant) weaken the electrostatic force between the ions and thereby decreases the tendency for the electro-valency to pass into covalency.

(iv) **Electronic configuration of the cations** : It has been observed that cations of  $18(s^2 p^6 d^{10})$  electrons in outermost shell can polarize more anion than cation having  $8(s^2 p^6)$  electrons in the outer most shell.



The  $d$ -electrons of 18 electrons shell screen the nuclear charge of the cation less effectively than the  $s$ - and  $p$ -electrons of the 2 electrons shell. Hence the 18 electron cations behaves as if they had a greater charge. Hence the melting point of  $\text{NaCl} (800^{\circ}\text{C})$  is greater than  $\text{CuCl} (442^{\circ}\text{C})$ . Similarly that for  $\text{KCl} (776^{\circ}\text{C}) > \text{AgCl} (445^{\circ}\text{C})$  and  $\text{RbCl} (715^{\circ}\text{C}) > \text{AuCl} (170^{\circ}\text{C}, \text{decomposes})$ .

### Application of the Concept of Polarization

Polarization power of a cation is generally represented by  $\phi$  and also known as ionic potential charge density. It can be represented as :

$$\phi = \text{charge on cation} / \text{radius of cation}.$$

The important applications of this concept are given below :

(i) **Character of a cation** : The larger the value of  $\phi$  the greater is the degree of covalency and its tendency to form complex compounds.

(ii) **Solvation energy** : When a substance is introduced into a solvent, the interaction that takes place is called solvation, and the energy change involved in this process may be denoted as solvation energy. If the solvent is water than it is known as hydration (hydration energy).

The larger the value of  $\phi$  for a cation, the greater is its tendency towards solvation. For example, the value of  $\phi$  decreases from  $\text{Li}^+$  to  $\text{Cs}^+$  in 1st group, therefore  $\text{LiCl}$  forms hydrated compounds such as  $\text{LiCl} \cdot 2\text{H}_2\text{O}$ ,  $\text{LiCl} \cdot 3\text{H}_2\text{O}$  etc. while other alkali ions do not form hydrated compounds. This is the reason that  $\text{LiCl}$  is soluble in organic solvents (pyridine etc.) while other halides are insoluble in organic solvents.

**(iii) Diagonal relationship :** Although the diagonal relationship can not be fully explained by the value of  $\phi$  even then it is very helpful in some extent e.g., the value of  $\phi$  for  $\text{Be}^{2+}$  and  $\text{Al}^{3+}$  is 6.4 and 6.0 respectively; therefore these elements exhibit diagonal relationship.

**(iv) Nature of oxides :** Covalent character of the  $\text{M}-\text{O}$  bond increases with the value of  $\phi$  [for the cation,  $\text{M}$ ] and at the same time the oxides will be acidic in nature. For example, covalent and acidic character is of the order :  $\text{Na}_2\text{O} < \text{MgO} < \text{Al}_2\text{O}_3$ , while their values of  $\phi$  is of the order:

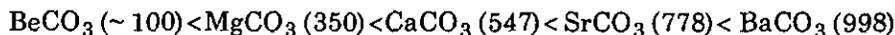
$$\phi_{\text{Na}^+} (1.05) < \phi_{\text{Mg}^{2+}} (3.08) < \phi_{\text{Al}^{3+}} (6.0)$$

$\text{Na}_2\text{O}$  is highly basic in nature while  $\text{Al}_2\text{O}_3$  is amphoteric in nature.

According to Carlidge,  $\text{M}_2\text{O}_n$  is basic when  $\sqrt{(\phi\text{M}^{n+})} < 2.2$ , is amphoteric when  $\sqrt{(\phi\text{M}^{n+})} = 2.2$  to  $3.2$  and is acidic when  $\sqrt{(\phi\text{M}^{n+})} > 3.2$ .

**(v) Nature of anhydrous halides :** The larger the value of  $\phi$  for a cation, the more covalent and non-conductor of electricity. If the value of  $\sqrt{\phi}$  for a cation is more than 2.2 the halide will be covalent and non-conductor of electricity. On the other hand if it is less than 2.2 the halide will be ionic and good conductor of electricity.

**(vi) Thermal stability of carbonates :** The larger the value of  $\phi$  for a bivalent cation, the lesser is its thermal stability. Because with increase in the value of  $\phi$  there will be strong pull on the electron cloud of the neighbouring oxygen atom of the carbonate get readily decomposed ( $^\circ\text{C}$ ) e.g.,



Similar reason may also be applied to the decomposition of sulphides, hydroxides, nitrates etc.

On the basis of above facts, we are considering some more examples regarding covalent nature of couple of the compounds. For example.

**(i)  $\text{CuO}$  and  $\text{CuS}$  :** Between  $\text{CuO}$  and  $\text{CuS}$ ;  $\text{CuS}$  is more covalent due to large size of  $\bar{\text{S}}$  as compared to  $\bar{\text{O}}$ .

**(ii)  $\text{AgCl}$  and  $\text{NaCl}$  :** Between  $\text{AgCl}$  and  $\text{NaCl}$ ,  $\text{AgCl}$  is more covalent because the outermost shell of  $\text{Ag}^+$  ion contains 18 electrons whereas the outermost shell of  $\text{Na}^+$  contains 8 electrons. It is due to the smaller screening effect of  $d$ -electrons in  $\text{Ag}^+$  ion.

**(iii)  $\text{LiCl}$  and  $\text{KCl}$  :**  $\text{LiCl}$  is more covalent due to smaller size of  $\text{Li}^+$  ion as compared to  $\text{K}^+$  ion.

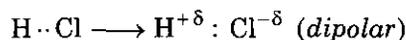
**(iv)  $\text{SnCl}_2$  and  $\text{SnCl}_4$  :**  $\text{SnCl}_4$  is more covalent due to more charge and small size of  $\text{Sn}^{4+}$  ion as compared to  $\text{Sn}^{2+}$  ion.

**(v)  $\text{AlCl}_3$  and  $\text{GaCl}_3$  :**  $\text{AlCl}_3$  is more covalent due to smaller size of  $\text{Al}^{3+}$  ion than  $\text{Ga}^{3+}$  ion.

**(vi)  $\text{NaCl}$  and  $\text{CuCl}$  :**  $\text{CuCl}$  is more covalent because  $\text{Cu}^+$  ion possesses 18 electrons in the outermost orbit. It is due to the fact that the screening effect of  $d$ -electrons is less than  $s$ - and  $p$ -electrons. Therefore  $\text{Cu}^+$  ion possesses  $18e^-$  in the outermost orbit and can polarise  $\text{Cl}^-$  ion more as compared to  $\text{Na}^+$  ion. Thus  $\text{CuCl}$  is more covalent than  $\text{NaCl}$ .

## • 2.17. DIPOLE MOMENT

It has been observed that if the two atoms linked by a chemical bond differ in their electronegativities, the more electronegative atom will get the negative charge and other will get a positive charge. In this state the molecule is said to possess a dipole moment. For example when HCl molecule is formed the shared pair of electrons is drawn near Cl, leaving a small positive charge (+ $q$ ) on the H atom and a small negative charge (- $q$ ) on the Cl atom. The molecule becomes dipoles ( $H^+ Cl^-$ ) on account of the relative displacement of centres of positive and negative electric charge on it. Such a molecule has a dipole moment and has equal positive (+ $q$ ) and negative (- $q$ ) charges separated by the distance,  $d$ .



Hence the dipole moment,  $\mu$ , may be defined as :

*"The vector equal in magnitude to the product of the electric charge,  $q$  and the distance,  $d$  having the direction of the line joining the positive and negative centres."*

Dipole moment = Electric charge  $\times$  Distance.

i.e., 
$$\mu = q \times d$$

The dipole moment,  $\mu$  is generally expressed in terms of e.s.u. or the Debye unit (D). Since for an electron,  $q$  is  $4.8025 \times 10^{-10}$  e.s.u. and internuclear distance  $d$  is of the order of  $10^{-8}$  cm., the value of the dipole moment is of the order of  $10^{-18}$  e.s.u. cm. or Debye.

In S.I. units  $e$  and  $d$  are of the order of  $1.6 \times 10^{-19}$  C and  $10^{-10}$  m respectively. Hence  $\mu$  is of the order  $10^{-19} \times 10^{-10} = 10^{-29}$  m C (metre Coulomb). Therefore

$$4.8 \times 10^{-18} \text{ e.s.u. cm} = 4.8 \text{ D}$$

$$1.6 \times 10^{-29} \text{ Cm} = 4.8 \text{ D}$$

$$0.33 \times 10^{-29} \text{ Cm} = 1 \text{ D}$$

The following methods can be used to determine the dipole moment of the molecules:

- (i) Temperature method
- (ii) Ebert's method
- (iii) Molar refraction method.

### Applications of Dipole Moment

**1. Calculation of Ionic Character :** In case of diatomic molecules, the measured dipole moment gives information on the displacement of the centre of the negative and positive charges. As discussed above,

$$\% \text{ Ionic character} = \frac{\mu_{\text{obs.}}}{\mu_{\text{ionic}}} \times 100$$

**Example 5.** In the HCl molecule,  $d_{HCl}$  is 1.27 Å. The dipole moment of gaseous HCl is  $0.347 \times 10^{-29}$  m C. Calculate % ionic character of the bond.

**Solution.** For 100% ionic bond,

$$\begin{aligned} \mu &= q \times d \\ &= 1.6 \times 10^{-19} \text{ C} \times 1.27 \times 10^{-10} \text{ m} \\ &= 2.032 \times 10^{-29} \text{ m C} \end{aligned}$$

$$\% \text{ Ionic character} = \frac{\text{Observed dipole moment} \times 100}{\text{Dipole moment for 100\% ionic bond}}$$

$$= \frac{0.347 \times 10^{-29} \text{ m C}}{2.032 \times 10^{-29} \text{ m C}} \times 100$$

$$= 17.07\%$$

## 2. Insight Geometry :

(i) **Bond Moment** : For polyatomic molecule, it is customary to understand the molecular dipole moment in terms of the contribution of the individual bonds of the molecules. The contribution of individual bond is called the bond moment. The method of calculating bond moment is given below :

The measured dipole moment of water is 1.85 D. The dipole moment is the vectorial sum of the individual bond moments of two — OH bonds directed at an angle of 104.5° with respect to each other.

$$\therefore \mu = [\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cos \theta]^{1/2}$$

$$\therefore \mu_{\text{obs}} = [\mu_{\text{OH}}^2 + \mu_{\text{OH}}^2 + 2\mu_{\text{OH}}^2 \cos 104.5^\circ]^{1/2}$$

$$1.85 = \mu_{\text{OH}} \sqrt{2} [1 + \cos 104.5]^{1/2}$$

$$\text{or } \mu_{\text{OH}} = \frac{1.85}{\sqrt{2} \times \sqrt{0.75}} = 1.51$$

The bond moments of some common bonds are given below :

H—F	H—Cl	H—Br	H—I
1.9 D	1.1 D	0.8 D	0.4 D
C—F	C—Cl	C—Br	C—I
1.4 D	1.5 D	1.4 D	1.2 D
H—O	H—N	H—C	
1.5 D	1.3 D	0.4 D	

(ii) **Bond Polarity** : Dipole moment indicates the polar character of the bond since the dipole moment in case of HF, HCl, HBr and HI decreases from HF to HI. This indicates that the polarity of the H—X bond decreases progressively from HF to HI.

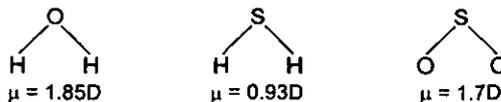
## 3. Geometry of the Molecules

A molecule is polar or non-polar depends also upon the arrangement of atoms in the molecules i.e., upon bond angles and the bond length of the molecule. Various examples are given here :

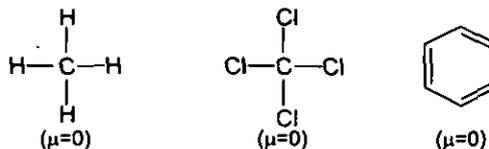
(i) Triatomic molecules of the compounds (e.g., CO<sub>2</sub>, CS<sub>2</sub>, C<sub>6</sub>H<sub>5</sub>—Hg—C<sub>6</sub>H<sub>5</sub>) have no dipole moment and thus have a linear structure.



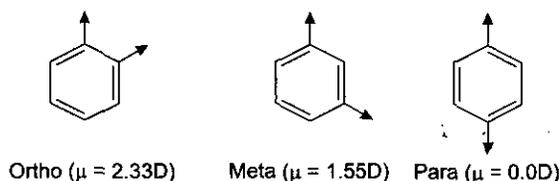
(ii) Water, hydrogen sulphide, sulphur dioxide etc. have definite dipole moments showing that they are not linear molecules. They have a triangular structure.



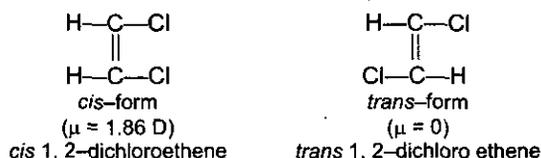
(iii) Methane, carbon tetrachloride, benzene have dipole moment zero indicating a symmetry in their molecules.



(iv) Disubstituted products of benzene (*o*-, *m*- and *p*-) have different dipole moments. *p*-Dichlorobenzene has zero dipole moment while the values for *o*- and *m*- products are 2.33 and 1.55 D respectively, and value of dipole moment of monochlorobenzene is 1.55 D.



(v) For geometrical isomers, the dipole moment of the *cis*-isomer has a higher value than the more symmetrical *trans* isomer. For example *cis*-1,2-dichloro ethene has a dipole moment, but in the *trans* form, the effective produced in one half of the molecule will be cancelled by that in the other half of the molecule and thus it will have zero dipole moment.



**4. Calculation of bond angle between two bonds :** When two or more bond moments constitute the dipole moment of the molecule, dipole moment is calculated by the vector sum of all the groups or bond moments :

$$\mu^2 = \mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cos \theta$$

where  $\mu$  is the resultant dipole moment of the molecule,  $\mu_1$  and  $\mu_2$  are the dipole moments of the two groups or bonds and  $\theta$  is the angle between them.

**Example 6.** The dipole moment of methyl alcohol ( $\text{CH}_3\text{OH}$ ) is 1.56 D. Calculate the bond angle HOC. The bond moments are as follows :

$$\mu_{\text{H}-\text{C}} = 0.4D, \mu_{\text{C}-\text{O}} = 0.7D \text{ and } \mu_{\text{H}-\text{O}} = 1.5D$$

**Solution.** The structure of  $\text{CH}_3\text{OH}$  may be shown as :

Here,

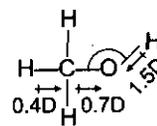
$$\mu_{\text{H}-\text{C}} = (0.4 + 0.7) = 1.1D \text{ and } \mu_2 = 1.5D$$

$$\therefore \mu = [\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cos \theta]^{1/2}$$

$$1.56D = [(1.1)^2 + (1.5)^2 + 2(1.1)(1.5) \cos \theta]^{1/2}$$

$$2.4336 = 3.46 + 3.3 \cos \theta$$

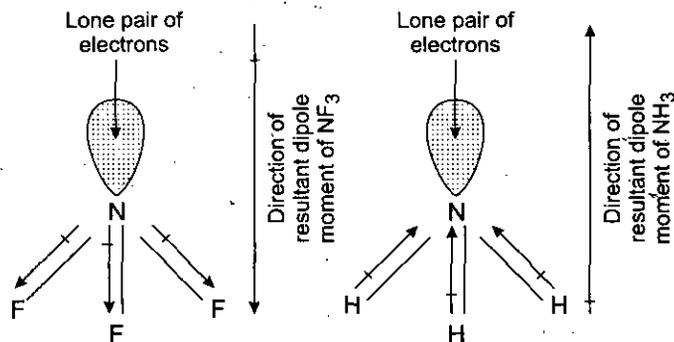
$$\text{or } \cos \theta = 0.311 \text{ or } \theta = 110^\circ$$



The dipole moment of  $\text{NH}_3$  molecule is considerably higher than that of  $\text{NF}_3$  molecule. Although the difference of electronegativities between the atoms in the respective bonds are almost identical. Explain

**Explanation :** Since F-atom is more electronegative than N-atom hence the direction of the three dipoles of the three N-F bonds in  $\text{NF}_3$  molecule are towards F-atom ( $\text{N} \rightarrow \text{F}$ ) and thus oppose the effect of the lone pair of electrons on N-atom. While in the case of  $\text{NH}_3$  the direction of three dipoles of the three N-H bonds are towards N-atom ( $\text{H} \rightarrow \text{N}$ ) and thus are added to the effect of the lone pair of electrons on N-atom. Consequently the resultant dipole moment of  $\text{NH}_3$  is towards the lone pair of electrons and becomes greater than that of  $\text{NF}_3$  molecule.

The above statement may be represented as follows :



Representation of direction of resultant dipole of  $\text{NF}_3$  and  $\text{NH}_3$  molecules.

• 2.18. IONIC CHARACTER

The percentage ionic character of a polar covalent bond depends upon following two factors :

(i) **Electronegativity differences of the bonded atoms** : According to Pauling percentage ionic character of binary compound may be given as :

$$\text{Percentage ionic character} = [1 - e^{0.25(x_A - x_B)}] \%$$

or

$$= [18(x_A - x_B)^{1.4}] \%$$

where  $x_A$  and  $x_B$  are the electronegativities of atoms A and B respectively. Hence the difference in the electronegativities amounts to 1.7 the bond is 50% ionic in character. If the difference is less than 1.7, the bond is more covalent in character, if the difference is more than 1.7 the bond is more ionic in character. The following relation may be given between difference of electronegativities ( $x_A - x_B$ ) and percentage of ionic character :

$x_A - x_B$	0.6	1.0	1.4	1.7	2.0	2.4	3.0	3.2
% Ionic character	9	22	39	51	63	76	91	92

Hannary-Smith (1946) proposed following equation for degree of ionic character for a non-polar AB molecule :

$$\text{Percentage ionic character} = [16(x_A - x_B) + 3.5(x_A - x_B)^2] \%$$

where  $x_A$  and  $x_B$  are the electronegativities of the elements A and B respectively.

**Example 7.** Calculate the percentage ionic character in gaseous HF, HCl, HBr and HI molecules. Given that  $x_H = 2.2, x_F = 4.0, x_{Cl} = 3.2, x_{Br} = 3.0$  and  $x_I = 2.7$ .

**Solution.** According to Pauling's equation;

$$\text{Percentage ionic character} = 18(x_A - x_B)^{1.4}$$

$$\therefore \text{For HF molecule} = 18[4.0 - 2.2]^{1.4} = 41\%$$

$$\text{HCl molecule} = 18[3.2 - 2.2]^{1.4} = 18\%$$

$$\text{HBr molecule} = 18[3.0 - 2.2]^{1.4} = 13.2\%$$

$$\text{HI molecule} = 18[2.7 - 2.2]^{1.4} = 6.8\%$$

According to Hannary and Smith equation :

$$\text{Percentage ionic character} = [16(x_A - x_B) + 3.5(x_A - x_B)^2] \%$$

$$\therefore \text{For HF molecule} = [16(4.0 - 2.2) + 3.5(4.0 - 2.2)^2] = 40.1\%$$

$$\text{HCl molecule} = [16(3.2 - 2.2) + 3.5(3.2 - 2.2)^2] = 19.5\%$$

$$\text{HBr molecule} = [16(3.0 - 2.2) + 3.5(3.0 - 2.2)^2] = 15.0\%$$

$$\text{HI molecule} = [16(2.7 - 2.2) + 3.5(2.7 - 2.2)^2] = 8.9\%$$

It is clear that both these results are comparable. Since in all these cases percentage ionic character is less than 50% hence all these molecules are covalent in nature in gaseous state and this character increases from HF to HI.

(ii) **Dipole moment of the polar molecule** : Dipole moment ( $\mu$ ) is an another good method to calculate the percentage ionic character of a diatomic molecule. According to this method,

$$\begin{aligned} \text{Percentage ionic character} &= \frac{\text{Observed dipole moment} \times 100}{\text{Dipole moment of ionic compound}} \\ &= \frac{\mu_{\text{obs}} \times 100}{\text{Distance} \times \text{Electronic charge}} \end{aligned}$$

## • SUMMARY

- **Formation of ionic bond** depends upon electron affinity, ionization energy and lattice energy.
- **Ions** are of two types cation and anion. The size of the cation is smaller than that of atom and the size of the anion is greater than that of atom.
- **Radius ratio rule** is helpful to decide the structure of the ionic crystal.
- **Lattice energy** of a ionic crystal can be calculated by Born-Landé's equation.
- **Enthalpy of formation of ionic compounds** can be calculated by Born-Haber's cycle.

$$\Delta H_f = S + D + I + E + U$$

(All the terms have usual meaning)

- **Solvation energy** of the ionic compounds depends upon hydration energy and lattice energy of the ionic compound.
- **Formation of covalent compounds** may be explained by VBT and MOT.
- **Heitler and London** put forward VBT. It was extended by **Pauling and Slater** accordingly the covalent bond is formed by the overlapping of the atomic orbitals.
- **Hybridisation** is an important phenomenon to explain the formation of covalent compounds. It is of different types e.g.,  $sp$ ,  $sp^2$ ,  $sp^3$ ,  $sp^3d$ ,  $sp^3d^2$  and  $sp^3d^3$ .
- **Bent's rule** may be stated as, 'More electronegative substituents prefer hybrid orbitals having less  $s$ -character and more electropositive substituents prefer hybrid orbitals having more  $s$ -characters'.
- **Resonance** is the description of the electronic structure of molecule (ion) by means of several schemes of pairing electrons with features of each scheme contributing to final description.
- According to MOT the AOs combine and form a resultant orbital known as the molecular orbital in which the identity of both the AOs is lost. We get BMO and ABMO by LCAO.
- As the B.O. increases stability of the bond increases and bond length decreases.
- The energy level of different MOs increases as  

$$\sigma(1s) < \sigma^*(1s) < \sigma(2s) < \sigma^*(2s) < \sigma(2p_z) < [\pi(2p_x) = \pi(2p_y)] < [\pi^*(2p_x) = \pi^*(2p_y)] < \sigma^*(2p_z)$$
- But due to mixing of the A.O.'s (in  $O_2$ ,  $F_2$  etc.) the order is  

$$\sigma(1s) < \sigma^*(1s) < \sigma(2s) < \sigma^*(2s) < [\pi(2p_x) = \pi(2p_y)] < \sigma(2p_z) < [\pi^*(2p_x) = \pi^*(2p_y)] < \sigma^*(2p_z)$$
- **Formal charge** on an atom in a molecule can be calculated as :

$$\theta_f = N_A - N_{lp} - \frac{1}{2}N_{bp}$$

- According to **VSEPR theory** the order of repulsion is  

$$lp - lp > lp - bp > bp - bp$$
 It is helpful in deciding the structure of the molecules.
- In multiple bonds first  $\sigma$ -bond is formed after that  $\pi$ -bond(s) is (are) formed.
- **Bond length** in a molecule AB may be given as :  

$$d_{A-B} = r_A + r_B - 0.09(\chi_A - \chi_B)$$
- **Bond length** depends upon : bond order, electronegativity, hybridisation and resonance.
- **Fajan's rules** are based of power of polarisation of cation.
- Dipole moment = Electric charge  $\times$  Distance [ $\mu = e \times d$ ]. Its unit is Debye ( $D$ ).
- **Ionic character** of the bond may be calculated by dipole moment or electronegativity.

• STUDENT ACTIVITY

1. Discuss the conditions for ionic bond formation and characteristics of ionic compounds.  
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2. What is radius ratio rule ? Describe its applications.  
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3. Derive Born-Lande's equation.  
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4. Discuss V.B. T. in brief.  
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5. Describe MOT in brief.  
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6. What do you mean by hybridisation.  
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7. Write the principles of resonance.  
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8. Describe the M.O. diagram of NO and CO molecules.  
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9. What is formal charge ? Calculate the formal charges of the atoms in sulphate ion.  
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10. Describe VSEPR Theory.  
.....  
.....  
.....
11. What do you mean by  $\sigma$  and  $\pi$ -bonds ? Give suitable examples.  
.....  
.....  
.....

.....  
 .....  
 12. Discuss dipole moment along with its applications.  
 .....  
 .....  
 .....

### • TEST YOURSELF

#### Answers the following questions :

1. What do you know about ionic bonds ? Write its characteristic properties and formation of cations and anions.
2. What are limiting radius ratio and radius ratio rule ? Discuss the limitations of this rule.
3. Discuss lattice energy of ionic solids. Derive Born-Landé's equation.
4. What is the covalent bond ? Write its characteristic properties. Draw the Lewis structure of  $N_2$ ,  $C_2H_4$  and  $C_2H_6$ .
5. What is valence bond theory ? Write its limitations also.
6. How can you describe the directional nature of covalent bond according to Pauling and Slater ?
7. What are sigma and pi bonds ? Compare them.
8. What do you know about hybridization ? Describe its rules.
9. Describe resonance and its principles. What is resonance energy ?
10. How does  $s$ -,  $p$ - and  $d$ -orbitals hybridize ? Give their examples.
11. What is VSEPR theory ? Describe its rules and limitations.
12. Describe the structure of any three compounds of the following, on the basis of VSEPR theory.  
 $NH_3$ ,  $H_2O$ ,  $SF_4$  and  $ClF_3$  as well as  $H_3O^+$  and  $ICl_2^-$  ions.
13. Discuss radius ratio rule. How do you calculate lattice energy of NaCl by Born-Haber cycle ?
14. What is molecular orbital theory ? Differentiate between atomic and molecular orbitals ?
15. Explain the formation of bonding and antibonding molecular orbitals according to LCAO with figures.
16. Draw the molecular orbital diagram of  $N_2$  and NO molecules. Calculate their bond order.
17. Draw the molecular orbital diagram of  $O_2$ ,  $O_2^-$  and  $O_2^+$ . Calculate their bond order.
18. Draw molecular orbital diagram for CO and NO molecules. Calculate their bond order.
19. What is dipole moment ? How can you calculate the ionic nature of the bond by dipole moment ?
20. Write short notes on the following :
  - (i) Madelung constant
  - (ii) Tetrahedral and octahedral interstices
  - (iii) Shape of the  $SF_4$  and  $XeF_2$
  - (iv) Differences between BMO and ABMO
  - (v) Polarity of the bond
  - (vi) Solvation energy
21. The following species possess highest bond order :
 

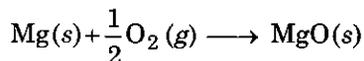
(a) $O_2$	(b) $O_2^+$	(c) $O_2^-$	(d) $O_2^{=}$
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22. Choose the correct bond order sequence :

- (a)  $O_2^+ > O_2^{2-} > O_2$  (b)  $O_2^+ > O_2 > O_2^-$   
(c)  $O_2^- > O_2 > O_2^+$  (d)  $O_2^- > O_2^+ > O_2$
23. Which one of the following molecules contains one unpaired electrons ?  
(a) NO (b) CO (c)  $N_2$  (d)  $O_2$
24. Oxygen molecule is paramagnetic, because :  
(a) It contains unpaired electrons (b) There is no charge  
(c) It contains paired electrons (d) It contains double bond
25. Choose the molecule which possess highest dipole moment :  
(a)  $NH_3$  (b)  $PH_3$  (c)  $AsH_3$  (d)  $SbH_3$
26. Acetylene molecule consists :  
(a)  $3\sigma$  and  $2\pi$  bonds (b)  $2\sigma$  and  $1\pi$  bonds  
(c)  $2\sigma$  and  $2\pi$  bonds (d)  $2\sigma$  and  $3\pi$  bonds
27.  $Na_2SO_4$  is soluble in water but  $BaSO_4$  is less soluble in water. Because :  
(a) The hydration energy of  $Na_2SO_4$  is lower than its lattice energy.  
(b) The lattice energy of  $BaSO_4$  is greater than its hydration energy.  
(c) There is no importance of lattice energy in solubility.  
(d) The hydration energy of  $BaSO_4$  is higher than its lattice energy.
28. Carbon atoms exhibit following hybridizations in diamond, graphite and acetylene respectively :  
(a)  $sp^2, sp, sp^2$  (b)  $sp^2, sp^2, sp$   
(c)  $sp^3, sp^2, sp$  (d)  $sp, sp^2, sp^3$
29. The central atom of  $BF_3$  molecule exhibits geometry and hybridization as follows  
(a) Linear and  $sp$  (b) Triangular and  $sp^2$   
(c) Tetrahedral and  $sp^3$  (d) Pyramidal and  $sp^3$
30. 1, 3-Butadiene consists :  
(a) Only  $sp$ -hybridized carbon atoms  
(b) Only  $sp^2$ -hybridized carbon atoms  
(c)  $sp$ - and  $sp^2$ -hybridized carbon atoms  
(d)  $sp$ -,  $sp^2$ - and  $sp^3$ -hybridized carbon atoms
31. Fill in the Blanks  
(i) In the nitrogen molecule the energy of  $\sigma(2p_z)$  orbital is ..... than that of  $\pi(2p_x)$  orbital.  
(ii) According to MOT, the paramagnetic character of  $O_2$  molecule is due to ..... unpaired electrons.  
(iii)  $O_2^-$  ion is ..... stable than  $O_2^+$  ion.  
(iii) The shape of  $NH_3$  molecule is .....  
(iv) In  $SF_6$  molecule sulphur exhibits ..... hybridization.  
(v)  $BF_3$  is a ..... molecule and bond angle is .....  
(vi) In a diatomic molecule on increasing bond order, then bond energy ..... and bond length .....
32. Choose True (T) and False (F) Statements  
(i) Antibonding molecular orbitals stabilizes the molecule.  
(ii) The bond order of  $NO^+$  is three.  
(iii) All molecules with polar bonds have dipole moment.  
(iv)  $sp^2$  hybrid orbitals have equal  $s$  and  $p$  character.  
(v) Oxygen atom exhibits  $sp^3$  hybridization in water molecule.  
(vi)  $XeF_2$  in a linear molecule in which Xe exhibits  $sp$ -hybridization.
33. Arrange the following in increasing order as given in bracket  
(i)  $BeSO_4, MgSO_4, CaSO_4, SrSO_4$  (Thermal stability)

- |  |                    |
|--|--------------------|
| (ii) $\text{H}_2\text{O}$ , $\text{NH}_3$ , $\text{CO}_2$ , $\text{CH}_4$  | (Bond angle)       |
| (iii) $\text{O}_2$ , $\text{O}_2^-$ , $\text{O}_2^+$ , $\text{O}_2^-$      | (Bond length)      |
| (iv) $\text{BeCl}_2$ , $\text{MgCl}_2$ , $\text{CaCl}_2$ , $\text{SrCl}_2$ | (Melting point)    |
| (v) $\text{Na}^+$ , $\text{Mg}^{2+}$ , $\text{Al}^{3+}$                    | (Polarising power) |
| (vi) $\text{CuCl}$ , $\text{NaCl}$   | (Covalent nature)  |

### 34. Numerical Questions

- (i) Calculate the heat of formation of sodium fluoride. If the sublimation energy and ionization energy of sodium are 108.7 and 497.7  $\text{kJ mol}^{-1}$  respectively. The dissociation energy and electron affinity of fluorine are 156 and 322  $\text{kJ mol}^{-1}$  respectively. The lattice energy of sodium fluoride is 900.4  $\text{kJ mol}^{-1}$ .
- (ii) Magnesium oxide is prepared as :



The sublimation energy and ionisation energy for two electrons are 152.7 and 2178  $\text{kJ mol}^{-1}$  respectively. The dissociation energy and electron affinity for two electrons are 495.4 and  $-744.7 \text{ kJ mol}^{-1}$  respectively. The lattice energy of MgO is 3933  $\text{kJ mol}^{-1}$ .

Draw Born-Haber's cycle diagram for this reaction and calculate the heat of formation of MgO.

- (iii) The internuclear distance in HCl molecule is 127 pm, and its dipole moment is  $3.44 \times 10^{-30} \text{ C m}$ . Calculate the ionic charge of the bond (charge on electron =  $1.6 \times 10^{-19} \text{ C}$ ).

## ANSWERS

21. (b) 22. (b) 23. (a) 24. (a) 25. (a) 26. (a) 27. (b) 28. (c) 29. (b) 30. (b)  
 31. (i) lower, (ii) two, (iii) less, (iv)  $sp^3d^2$ , (v) triangular,  $120^\circ$ , (vi) increases, decreases.  
 32. (i) F, (ii) T, (iii) F, (iv) F, (v) T, (vi) F. 33. (i)  $\text{BeSO}_4 < \text{MgSO}_4 < \text{CaSO}_4 < \text{SrSO}_4$   
 (ii)  $\text{H}_2\text{O} < \text{NH}_3 < \text{CH}_4 < \text{CO}_2$  (iii)  $\text{O}_2^+ < \text{O}_2 < \text{O}_2^- < \text{O}_2^{2-}$  (iv)  $\text{BeCl}_2 < \text{MgCl}_2 < \text{CaCl}_2 < \text{SrCl}_2$   
 (v)  $\text{Na}^+ < \text{Mg}^{2+} < \text{Al}^{3+}$  (vi)  $\text{NaCl} < \text{CuCl}$  34. (i)  $-540 \text{ kJ mol}^{-1}$  (ii)  $-609.9 \text{ kJ mol}^{-1}$  (iii) 17%.

# UNIT

## 3

### FUNDAMENTALS OF ORGANIC CHEMISTRY AND STEREOCHEMISTRY

#### STRUCTURE

##### • FUNDAMENTALS OF ORGANIC CHEMISTRY

- Inductive Effect
- Electromeric Effect
- Resonance and Hyperconjugation
- Cleavage of Bonds
- Nucleophiles and Electrophiles
- Reactive Intermediates : Carbocations, Carboanions and Free Radicals
- Strength of Organic Acids and Bases
- Aromaticity

##### • STEREOCHEMISTRY

- Conformation
- Representation of Three-Dimensional Molecules
- Concept of Chirality
- Geometrical Isomerism
- Optical Isomerism
- CIP Rules : R/S and E/Z Nomenclature
- Summary
- Student Activity
- Test Yourself
- Answers

#### LEARNING OBJECTIVES

After going this unit you will learn :

- Inductive and electromeric effect along with their uses
- Resonance and hyperconjugation and their effects
- Cleavages of bonds and types of attacking reagents
- Reactions intermediates formed during the reactions
- Acidic and basic characters of the acids and bases
- Aromatic character of organic molecules
- Conformations of certain alkanes
- Stereoisomerism of organic molecules
- CIP rules

#### FUNDAMENTAL OF ORGANIC CHEMISTRY

In organic chemistry chemical reaction may be presented as :

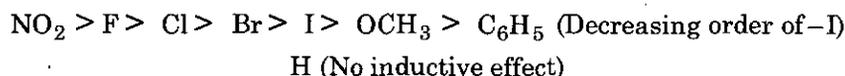


The reaction may or may not occur depending upon the density of electrons **at the site of reaction** in the substrate. The electron density in the substrate is **influenced by** inductive, electromeric and mesomeric effects.

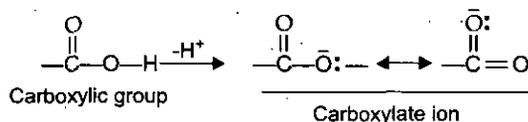
### • 3.1. INDUCTIVE EFFECT (I)

When a covalent bond is formed between similar atoms *e.g.*, H—H, Cl—Cl etc. the bonded electron pair is equally shared between the two atoms, hence the bond is *non-polar*. However a covalent bond formed between dissimilar atoms is *polar* since the sharing of electrons is not equal, the more electronegative part (atom) attracting a greater share, *e.g.* C → Cl bond. This displacement of bond electrons towards one direction is transmitted through the carbon atoms in a carbon chain and is called **inductive effect**. Atoms or groups which are more electronegative than hydrogen, exert **negative inductive effect (-I)** *i.e.*, they pull electrons towards themselves. On the other hand, if the atom or group is less electronegative than hydrogen, it exerts a **positive inductive effect (+I)**, *i.e.*, they repel or release electrons away from themselves.

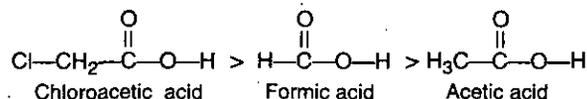
Some of the groups and atoms with their decreasing negative and positive inductive effects are given below :



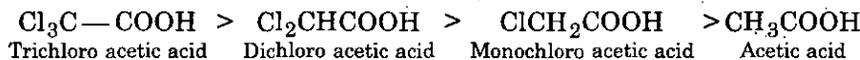
(a) **Acid strength** : An acid is a compound which releases  $\text{H}^+$  ion. Acid strength is, therefore, the ease with which  $\text{H}^+$  is released. Release of  $\text{H}^+$  always depends upon the stability of the anion formed. Thus carboxylic (organic) acids release  $\text{H}^+$  as the carboxylate ion stabilises due to dispersal of negative charge between two oxygen atoms.



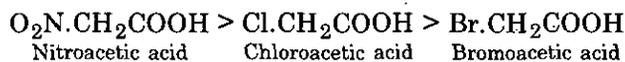
Any group or atom attached in a carboxylic acid can increase its acid strength if it shares the negative charge present on oxygen of its anion (It is possible due to the -I effect of groups or atoms). On the other hand, if an atom or group present in a carboxylic acid increases negative charge on the oxygen atoms of its anion, it makes the acid weakly acidic (It is possible due to +I effect of group or atom). Thus, **chloroacetic acid is stronger than formic acid** (-I effect of chlorine atom) **which in turn is stronger than acetic acid** (+I effect of methyl group).



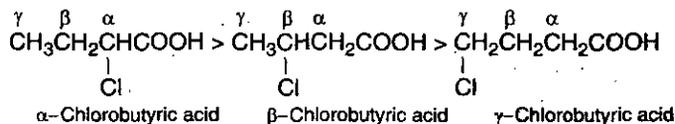
As the number of groups or atoms exerting -I effect increases in an acid, the strength of acid also increases. Thus, amongst the following acids, the decreasing order of acid strength is :



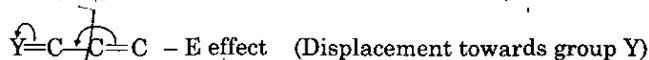
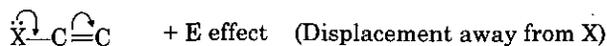
The acid strength of monosubstituted acids also depends on the -I effect of the substituent. A substituent with greater -I effect increases the acid strength, thus



The closer if the substituent, exerting -I effect to the carboxyl group, the stronger will be the acid. Thus,

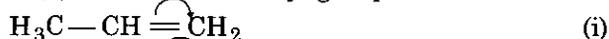




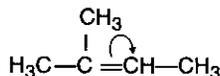


Some +E effect producing groups are  $-\text{F}$ ,  $-\text{Cl}$ ,  $-\text{Br}$ ,  $-\text{I}$ ,  $-\text{OH}$ ,  $-\text{OR}$ ,  $-\text{NR}_2$  etc. Some  $-E$  effect producing groups are  $=\text{NR}_2$ ,  $=\text{NHR}$ ,  $=\text{O}$  etc.

Actually, the displacement in the molecule would be to which side, depends upon (i) the nature of inductive effect of the substituent present and (ii) the relative stability of carbonium ion and carbanion formed, e.g., the displacement of electrons in propylene would be according to (i) and not (ii) due to  $+I$  of methyl group.



Similarly, the displacement of electrons in 2-methyl butene-2 is as given below, owing to relative stability of carbonium and carbanion formed.

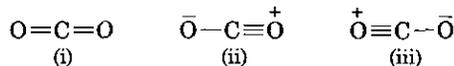


If a multiple bond is present between two dissimilar atoms, the displacement occurs always towards the more electronegative atom.



### • 3.3. RESONANCE

Sometimes, it is not possible to represent a molecule by a definite electronic structure which may be able to account for its observed properties. For example,  $\text{CO}_2$  may be represented by the following three electronic structures :



The observed C—O bond length is 1.15 Å for both bonds which is intermediate between those calculated for  $\text{C}=\text{O}$  (1.22 Å) and  $\text{C}\equiv\text{O}$  (1.10 Å). Thus, each of the bonds in  $\text{CO}_2$  molecule is a hybrid, i.e., intermediate between a double and triple bond. The observed heat of formation of  $\text{CO}_2$  molecule is 383 k.cal/mole, whereas calculated value for structure (i) is 346 k.cal/mol. In such cases, the actual structure of the compound cannot be written on paper although each structure makes some contribution to the actual structure of the compound.

*When several structures may be assumed to contribute to the actual structure of a compound but none of them can be said to represent it uniquely the compound is said to exhibit resonance. The individual structures are called as canonical or resonance forms and actual structure of the compound is said to be resonance hybrid of all the contributing structures.*

Resonance gives extra stability to the molecule. It is indicated by a double headed arrow ( $\leftrightarrow$ ) between the contributing structures.

#### [I] Conditions of Resonance

(i) All the canonical forms should have the same atomic positions. They should differ only in the positions of electrons.

(ii) All the canonical forms should have the same number of paired and unpaired electrons.

(iii) All the canonical forms should have almost equal energy.

#### [II] Characteristics of Resonance

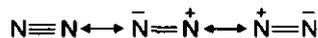
(i) The heat of formation of a resonance hybrid is more than calculated for any of its canonical forms. This difference of energy is known as resonance energy. Greater the *resonance energy*, greater is the stability of the molecule.

(ii) The bond distance in a resonance hybrid is different from the bond distance in canonical structure.

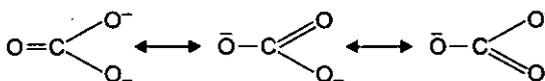
(iii) The dipole moment of the resonance hybrid is different from the value calculated for canonical structures.

### [III] Examples of Resonance

(i) Nitrogen



(ii) Carbonate ion

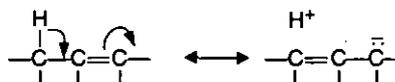


(iii) Benzene



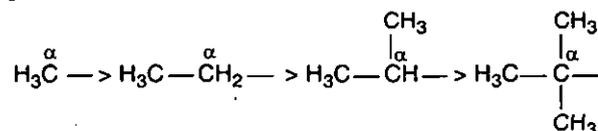
### • 3.4. HYPERCONJUGATION

We know that in inductive effect the electron release through +I effect by alkyl groups is in the order, *tertiary* > *secondary* > *primary*. This order is reversed, however, if the alkyl group is linked to an unsaturated carbon. Under these circumstances the release of electrons by an alkyl group is in the order, *primary* > *secondary* > *tertiary*. This is due to the weakening of C—H bond present near to unsaturated carbon e.g.,



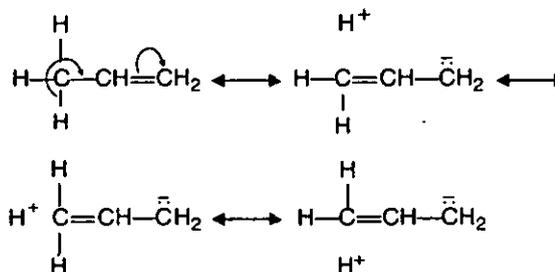
This mechanism of electron release is known as *hyperconjugation*. The effect is also known as **Baker-Nathan effect** (after the name of its discoverer), no-bond resonance (as no bond is shown between carbon and hydrogen in the resonating form) and  $\sigma - \pi$  conjugation.

As the interaction takes place between the  $\sigma$  electrons of carbon-hydrogen bond with  $\pi$  electrons of the double bond, it would be maximum if more hydrogen atoms are present on carbon near the double bond. Thus, the electron release amongst the following alkyl groups is in the order.



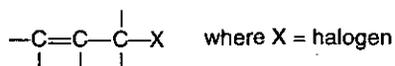
With 3- $\alpha$ -H-atoms    With 2- $\alpha$ -H-atoms    With 1- $\alpha$ -H-atoms    With no- $\alpha$ -H-atoms

The three hydrogen atoms of methyl group in propylene molecule contributes to this effect as shown below :



### [I] Reverse Hyperconjugation

The phenomenon of hyperconjugation is also observed in the following system :

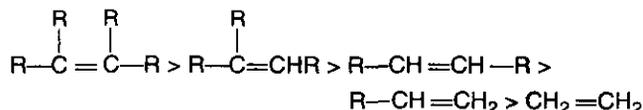


In this system, the migration of  $\pi$ -electrons takes place in the reverse direction, hence it is called as **reverse hyperconjugation**.

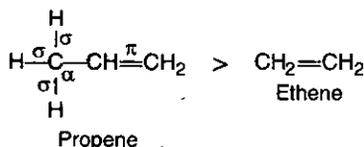


### [III] Effects of Hyperconjugation

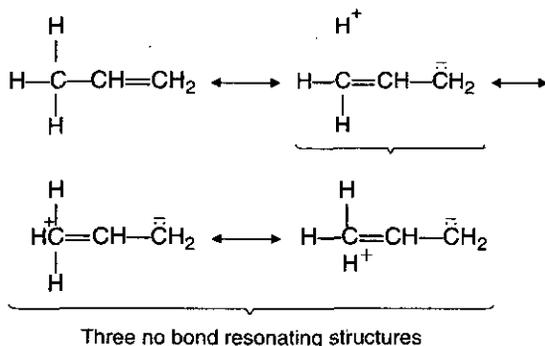
(1) **Stability of alkenes** : On the basis of this effect, the stability of different alkenes can be explained. The greater the number of alkyl groups attached to doubly bonded carbon atom, the more stable is the alkene. Thus, the decreasing order of stability of different alkenes can be represented as :



In an alkene, the greater the number of  $\alpha$ , C-H  $\sigma$ -bonds in conjugation with  $\pi$ -bond, more will be its no bond resonating forms. As a result is the stability of an alkene. For example, **propene is more stable than ethene**.

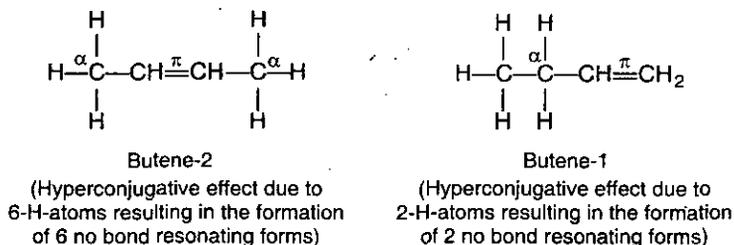


This is because in propene, three  $\alpha$ , C-H  $\sigma$ -bonds are present in conjugation with  $\pi$ -bond. Hence, three no bond resonating structures are possible in propene.

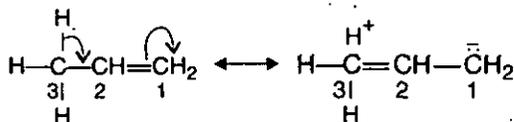


On the other hand, in ethene no C-H  $\sigma$ -bond is present in conjugation with  $\pi$ -bond. Hence, there is no bond resonating structure in ethene.

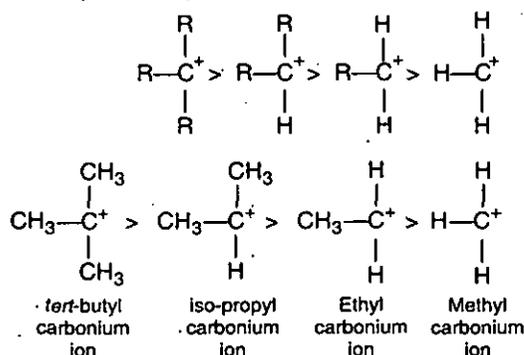
Hyperconjugative effect is used to explain as to why an alkene more substituted at unsaturated carbon is more stable than isomeric alkene with less substitution. Thus, **butene-2** is more stable than **butene-1**.



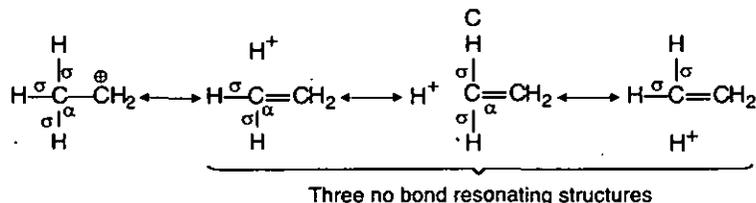
(2) **Bond lengths** : The bond lengths are changed due to hyperconjugation. For example, in  $\text{CH}_3-\text{CH}=\text{CH}_2$  (propene),  $\text{C}_2-\text{C}_3$  single bond acquires some double bond character. As a result, this bond length is found to be  $1.50\text{\AA}$ , whereas C—C single bond length is  $1.54\text{\AA}$ . Similarly,  $\text{C}_1-\text{C}_2$  bond length is found to be greater than  $1.34\text{\AA}$ .



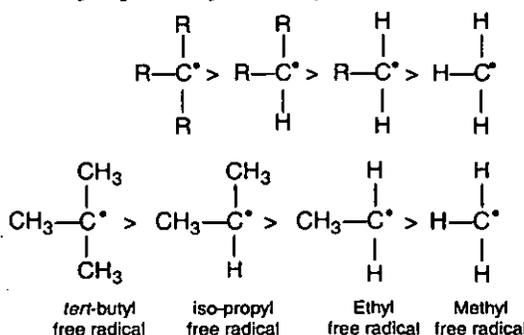
(3) **Stability of carbonium ions** : The stability of carbonium ions is in the order **tertiary > secondary > primary > methyl.**



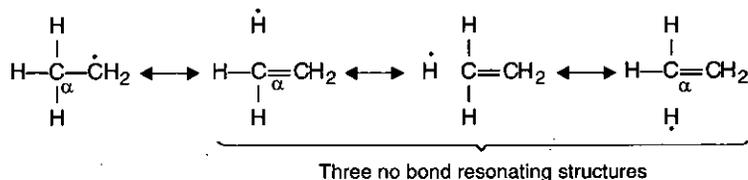
This can be explained on the basis of hyperconjugation. In the carbonium ions, C—H bond is attached to a carbon which has a vacant *p*-orbital. As a result, migration of  $\sigma$ -electrons takes place due to hyperconjugation. The tert-butyl carbonium ion contains 9  $\alpha$ , C—H  $\sigma$ -bonds, isopropyl carbonium ion contains 6  $\alpha$ , C—H  $\sigma$ -bonds, isopropyl carbonium ion contains 3  $\alpha$ , C—H  $\sigma$ -bonds and methyl carbonium ion does not contain any  $\alpha$ , C—H  $\sigma$ -bond. Hence, these have 9, 6, 3 and 0 no bond resonating structures respectively due to hyperconjugation. The greater the number of bond resonating structures of a carbonium ion, greater is its stability. For example, ethyl carbonium ion has the following three no bond resonating structures :



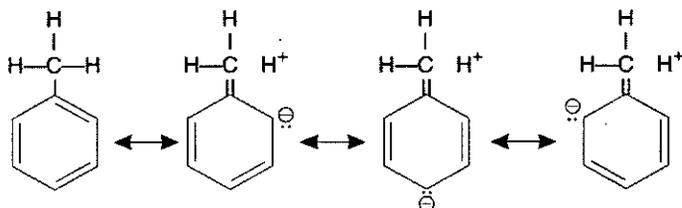
(4) **Stability of organic free radicals** : The stability of organic free radicals is in the order, **tertiary > secondary > primary > methyl.**



This can be explained on the basis of hyperconjugation. In the organic free radicals, C—H bond is attached to a carbon which has a partially filled *p*-orbital. As a result, migration of  $\sigma$ -electrons takes place due to hyperconjugation. The tert-butyl free radical contains 9  $\alpha$ , C—H  $\sigma$ -bonds, iso-propyl free radical contains 6  $\alpha$ , C—H  $\sigma$ -bonds, ethyl free radical contains 3  $\alpha$ , C—H  $\sigma$ -bonds and methyl free radical does not contain any  $\alpha$ , C—H  $\sigma$ -bond. Hence, these have 9, 6, 3 and 0 no bond resonating structures, respectively due to hyperconjugation. The greater the number of no bond resonating structures of an organic free radical, greater is its stability. For example, ethyl free radical has the following three no bond resonating structures :

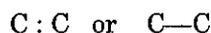


(5) **Directive influence of alkyl groups in aromatic substitution** : The directive influence of alkyl groups can be explained on the basis of hyperconjugation. The alkyl ( $\text{CH}_3-$ ,  $\text{C}_2\text{H}_5-$  etc.) group of alkylbenzene is ortho and para directing. In such compounds, the migration of electrons takes place in the benzene ring due to hyperconjugation so that electron density is increased at ortho and para positions. As a result, the electrophilic substitution takes place at ortho and para positions in these compounds.

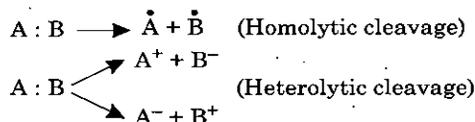


### • 3.5. CLEAVAGE OF BONDS

The covalent bond is formed by the sharing of electrons *e.g.*,



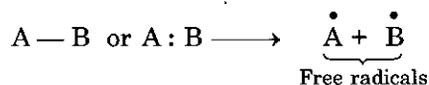
When the two electrons are separated from each other the process is said to be cleavage of bond or fission of bond. It can take place in two manners as :



Both of these are discussed here.

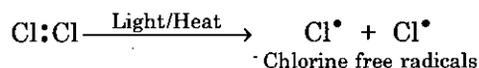
#### [I] Homolytic Fission

A covalent bond undergoes homolytic fission when each of the two separating atoms takes away one electron with one of the bonding pair of electrons.

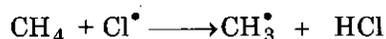


The two fragments, thus, produced carry an odd electron each and are called **free radicals**. These are unstable and at once react with other radicals or molecules by gaining one more electron to restore the stable bonding pair.

Homolytic fission proceeds to produce free radicals by the application of energy, may be heat or light. This type of fission generally takes place in gaseous reactions and explains the substitution reactions of alkanes. Consider the reaction of methane and chlorine to form methyl chloride. Firstly, homolytic fission of chlorine molecules takes place in the presence of ultraviolet light or by heat, resulting in free chlorine radicals which are highly reactive.



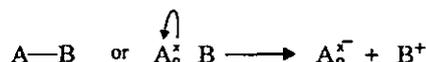
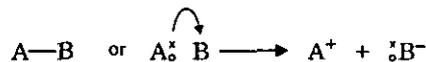
Methane then reacts with chlorine free radical to form methyl free radical ( $\text{CH}_3^\bullet$ ) which then combines with chlorine molecule to form methyl chloride ( $\text{CH}_3\text{Cl}$ ) and chlorine free radical.





### (II) Heterolytic Fission

When a covalent bond breaks in such a way that both the bonding electrons are taken away by one of the two separating atoms or groups, it is said to have undergone heterolytic fission.



The curved arrow points towards the atoms or groups that takes away both the shared electrons and, therefore, becomes negatively charged leaving behind the other positively charged atom or group. In general, the heterolytic bond fission yields one positive and one negative ion.

The course of heterolytic fission is determined by electronegativities of atoms or groups joined by covalent bonds. If B is more electronegative than A, then B will take away the bonding electron pair and fission will be according to course (i). If A is more electronegative than B, the fission will be according to course (ii).

Heterolytic fission is more common in organic reactions taking place in solutions. These reactions take place more readily in polar solvents like H<sub>2</sub>O and are catalysed by the presence of ionic catalysts.

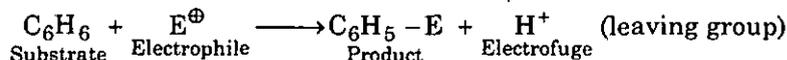
### • 3.6. TYPES OF REAGENTS

The completion of organic reactions depends, very much, on the nature of attacking reagents. The attacking reagents are generally of two types, viz., nucleophilic reagent (nucleophile, Nu<sup>-</sup>) and electrophilic reagent (electrophile, E<sup>+</sup>).

A reagent that brings an electron pair is called a nucleophile and the reaction is called nucleophilic reaction (SN). The leaving group is called nucleofuge e.g.,

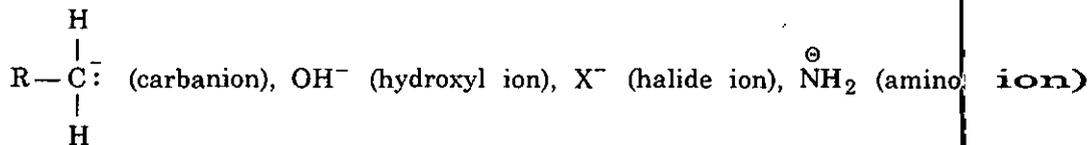


A reagent that takes an electron pair is called electrophiles and the reaction is called electrophilic reaction (SE). The leaving group is called electrofuge e.g.,



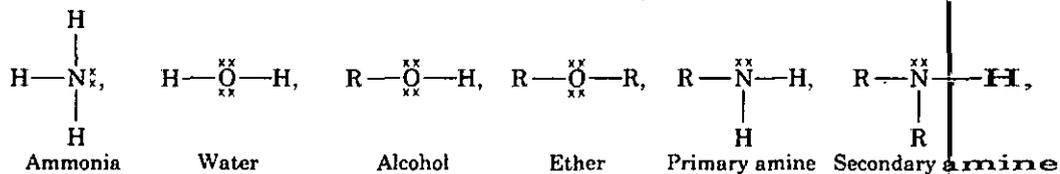
**(A) Nucleophilic Reagents :** The reagents which show the attraction towards nucleus are called nucleophilic reagents or nucleophiles (nucleo = nucleus, philic = loving). Since the nucleus is positively charged, these reagents will be negatively charged or electron rich substances. These are of two types :

**(a) Negative nucleophiles (Anions) :** These have an excess of electron pair and carry a negative charge. For example,

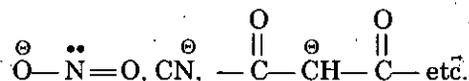


$\text{RO}^-$  (alkoxy ion).

**(b) Neutral nucleophiles :** These possess lone pair of electrons but no charge.



(c) **Ambident nucleophile** : The nucleophiles which can attack through two or more atoms are called **ambident nucleophile**. For example

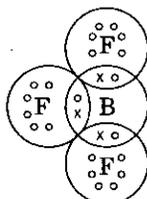


The nucleophiles may also be classified according to the kind of atom that forms a new covalent bond with carbon atom of the substrate. The most common nucleophiles are oxygen, nitrogen, sulphur, halogen and carbon nucleophiles.

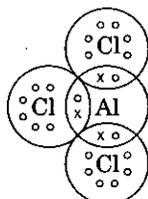
(B) **Electrophilic Reagents** : The reagents which show the attraction towards electrons are called **electrophilic reagents** or **electrophiles**. (electro = electron, philic = loving). These reagents are short of a pair of electrons than the stable one. These reagents are of two types :

(a) **Positive electrophiles** : These are deficient in two electrons and carry a positive charge, e.g.,  $\text{R}-\text{CH}_2^+$ ,  $\text{R}_2\text{CH}^+$ ,  $\text{R}_3\text{C}^+$  (carbonium ion),  $:\ddot{\text{Br}}^+$  (bromonium ion),  $\text{H}^+$  (hydrogenium ion),  $\text{H}_3\text{O}^+$  (hydronium ion),  $\text{NO}_2^+$  (nitronium ion),  $\text{SO}_3\text{H}^+$  (sulphonium ion),  $\text{NO}^+$  (nitrosylium ion) etc.

(b) **Neutral electrophiles** : In these, the central atom has six electrons but have no charge, e.g.,  $\text{BF}_3$  (boron trifluoride),  $\text{AlCl}_3$  (aluminium chloride),  $\text{SO}_2$  (sulphur dioxide),  $\text{SO}_3$  (sulphur trioxide),  $>\text{C}=\text{O}$  (carbonyl group),  $\text{ZnCl}_2$  (zinc chloride),  $\text{R}-\text{C} \begin{array}{l} \text{O} \\ // \\ \text{Cl} \end{array}$  (acid chloride),  $:\text{CH}_2$  (carbene) etc.



Boron trifluoride



Aluminium chloride

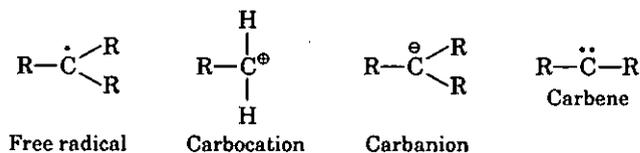
Both type of electrophiles can attack the ion or molecule which is electron rich.

#### Differences between electrophiles and nucleophiles

	Electrophiles	Nucleophiles
1.	These are electron deficient species.	1. These are electron rich species.
2.	These are generally cations.	2. These are generally anions.
3.	These are as Lewis acids.	3. These are as Lewis bases.
4.	These possess empty orbitals to accept the electrons.	4. These possess unshared electron pair which can be donated.
5.	These have low electron density.	5. These have high electron density.
6.	These are represented as $\overset{\oplus}{\text{E}}$ .	6. These are represented as $\overset{\ominus}{\text{Nu}}$ .

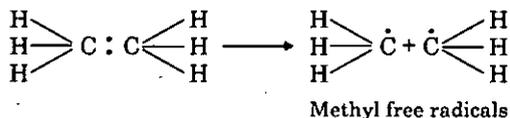
### • 3.7. REACTIVE INTERMEDIATES

Homolytic and heterolytic bond cleavage give rise to the formation of short lived species called reaction intermediates or reactive intermediate. These intermediates species are very reactive and quickly changed to more stable molecules. However, under certain circumstances, they are of sufficient stability to be isolated and studied. The most common types of reactive intermediates with less than four covalent bonds at carbon are the following :



### Free Radicals

A neutral atom or group of atoms which has an odd or unpaired electron is called a free radical, e.g., if a carbon-carbon bond of ethane breaks in homolytic manner, two methyl radicals are formed.



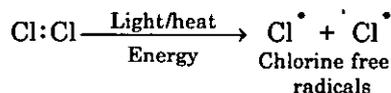
Free radicals are odd electron molecules e.g.,  $\dot{\text{C}}\text{H}_3$ ,  $\dot{\text{C}}_2\text{H}_5$ ,  $\dot{\text{C}}_6\text{H}_5$ ,  $(\text{C}_6\text{H}_5)_3\dot{\text{C}}$  etc.

### Characteristics of Free Radicals

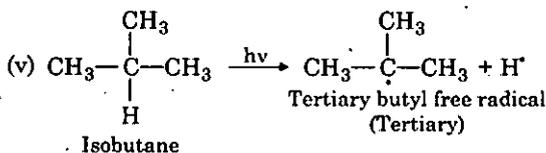
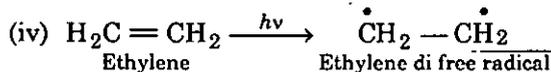
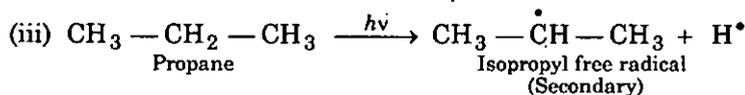
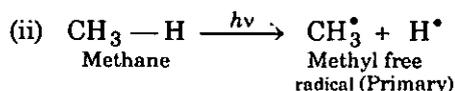
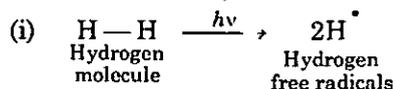
- (i) Free radicals are formed in presence of sunlight and when the reactants are in the gaseous state.
- (ii) They are highly unstable and reactive.
- (iii) They are highly unstable and immediately take an electron from a radical or molecule to form a stable bond.
- (iv) Free radicals are generally electrically neutral since the odd electron present on them is that electron which is used in the formation of a covalent bond.
- (v) The high reactivity of free radicals is due to the nature of odd electron to form a bond with any available electron.
- (vi) Free radicals are paramagnetic in nature, i.e., they are attracted by a magnetic field.

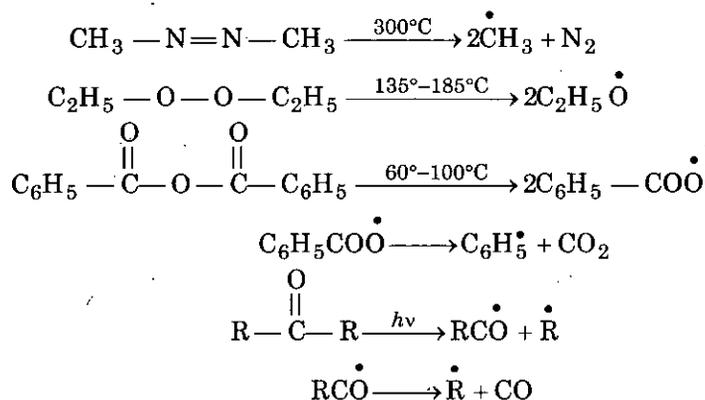
### Formation of Free Radicals

Formation of free radical is always initiated by energy (heat or light), e.g., a molecule of chlorine breaks into chlorine free radicals in presence of sunlight or on heating.



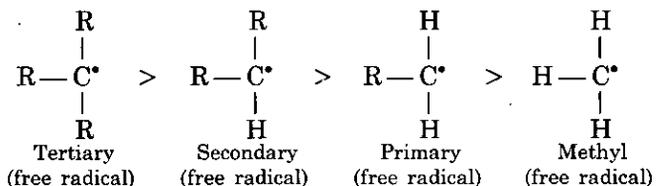
### Examples :



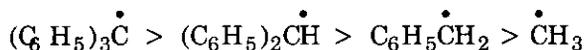


### Stability of Free Radicals

(1) The energy required for breaking the C—H bond is not always the same but it is generally different. To make  $\text{CH}_3\dot{\text{C}}$  from  $\text{CH}_4$ , the energy required is 102 kcal,  $\text{C}_2\text{H}_5\dot{\text{C}}$  from  $\text{C}_2\text{H}_6$ , the value is 97 kcal,  $\text{CH}_3 - \dot{\text{C}}\text{H} - \text{CH}_3$  from  $\text{C}_3\text{H}_8$ , the value is 94 kcal and to make  $(\text{CH}_3)_3\text{C}\dot{\text{C}}$  from  $(\text{CH}_3)_3\text{C}-\text{H}$ , the value is 91 kcal. So, electron repelling groups like methyl (alkyl) group increases the stability of free radicals. The order of stability of primary, secondary and tertiary free radicals is as follows :

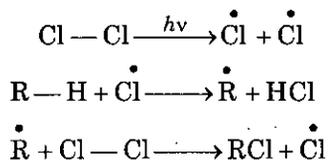


(2) Those free radicals which have resonance are comparatively more stable, e.g., phenyl free radical ( $\text{C}_6\text{H}_5\dot{\text{C}}$ ) is more stable than methyl free radical ( $\text{CH}_3\dot{\text{C}}$ ).  $\sigma$  electrons of a  $\alpha$  C—H bond can delocalise with the half filled p-orbital of the C-atom containing odd electron thus spreading the odd electron over all such bonds and thereby stabilising the radical upto some extent. The order of stability is,

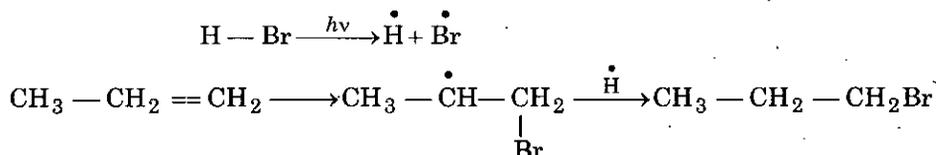


**Reactions of Free Radicals :** Some common reactions of free radicals are as follows :

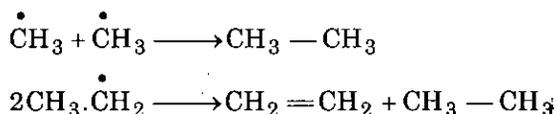
*Halogenation of alkanes :*



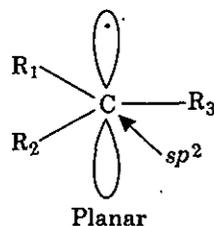
*Addition of HBr :*



*Combination and Disproportionation :*



**Structure :** In alkyl free radicals C-atom shows  $sp^2$ -hybridisation and shape of the free radical is planar as :



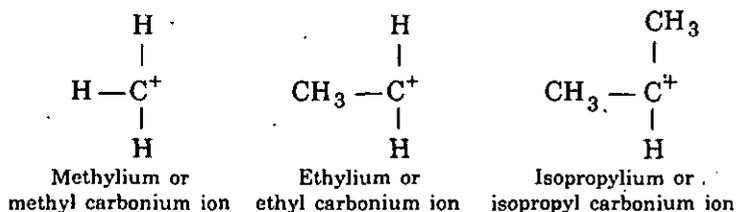
### Difference between a free radical and an ion

Characteristics		Free radicals	Ions
1.	Nature	These are electrically neutral. e.g., $\dot{\text{C}}\text{l}$ , $\dot{\text{C}}\text{H}_3$ , $\dot{\text{C}}_2\text{H}_5$ etc.	These contain either positive or negative charge e.g., $\text{CH}_3^+$ , $\text{Cl}^-$ , $\text{C}_2\text{H}_5^+$ , $\text{C}_2\text{H}_5^-$ etc.
2.	Magnetic property	These have one unpaired electron, so they are paramagnetic.	All the electrons are paired in ions, so they are diamagnetic.
3.	Hybridisation	The carbon atom of alkyl group on which unpaired electron is present is $sp^2$ hybridised.	Positively charged carbon atom is $sp^2$ hybridised, while negatively charged carbon atom is $sp^3$ hybridised.
4.	Method of preparation	These are formed by the homolytic fission of covalent bonds.	These are formed by the heterolytic fission of covalent bonds.

### Carbonium Ion

**Carbonium ion or carbo-cations :** An ion containing a positively charged carbon centre is called a carbonium ion or carbocations. These ions are named by adding the suffix 'ium' to the name of the parent alkyl group i.e., alkylum.

For example,



### Characteristics of Carbonium Ion

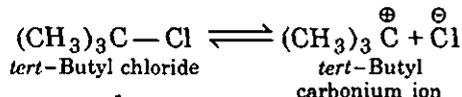
(1) All the carbonium ions are named by adding the suffix 'ium' to the name of the alkyl group present e.g.,  $\text{CH}_3^+$  (methylum) etc.

(2) The carbonium ions are very reactive. This is due to the fact that the central positively charged carbon in them has only six electrons in the outermost shell and they have a marked tendency to complete the octet. Hence, a carbonium ion combines readily with any substance that can donate a pair of electrons.

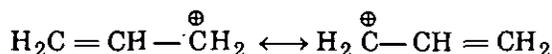
(3) Carbonium ion being deficient in electrons, is ordinarily very unstable. However, if an electron repelling group is present adjacent to positively charged carbon, the former neutralizes the positive charge.

### Formation of Carbonium Ions

(i) The carbonium ions are formed by the ionisation of halogen compounds, e.g.,

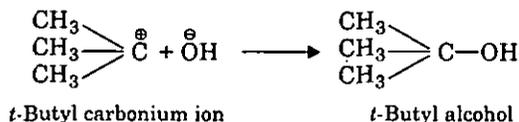




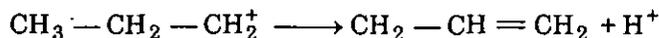


### Some Important Reactions Involving Carbonium Ions

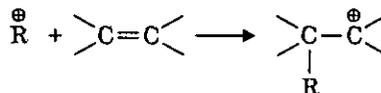
(i) Reaction with a nucleophilic reagent.



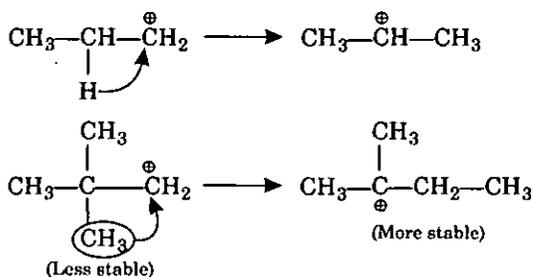
(ii) Separation of hydrogen proton to form an unsaturated molecule.



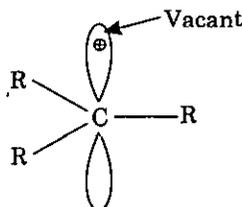
(iii) By the addition of carbonium ion to the  $\pi$  electrons of an unsaturated molecule.



(iv) Rearrangement reaction to form more carbonium ion, e.g.

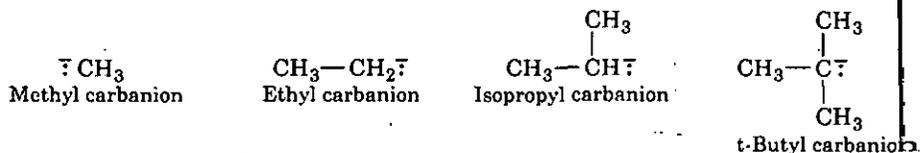


**Structure :** The carbon atom of carbocation shows  $sp^2$  hybridisation in which the  $p$ -orbital is devoid of any electron  $\oplus$ . Thus it has planar structure, with three  $\sigma$  bonds and bond angle  $120^\circ$  between them.



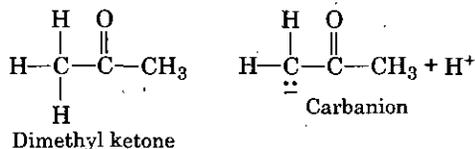
### Carbanion

An ion containing a negatively charged carbon centre is called as **carbanion**. These ions are named by adding the word carbanion to the parent alkyl group. For example,



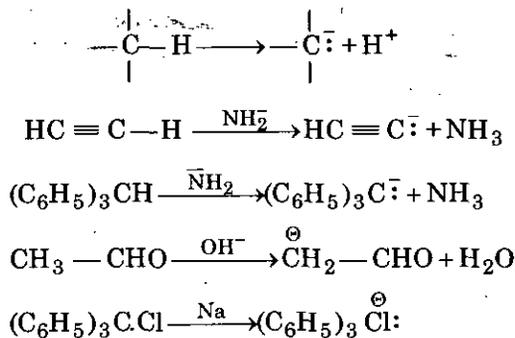
### Characteristics of Carbanions

- (1) Carbanions are named by writing the word carbanion after the name of alkyl group present in them as given above.
- (2) Though the carbon of the carbanions contains eight electrons (complete octet) even then they are highly reactive intermediates. They readily attach with electrophilic reagents (electrophiles).
- (3) In general, the carbanions are unstable, as they have a negative charge on carbon. However, the presence of some electronegative group ( $>\text{C}=\text{O}$ ,  $\text{C}\equiv\text{N}$  etc.) in the vicinity makes them stable.

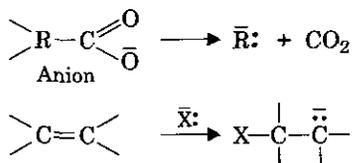


### Formation of Carbanions

Organic compounds which possess a labile or acidic hydrogen have a tendency to lose carbanions. In such cases, hydrogen breaks away as hydrogen proton bearing lone pair of electrons on the carbon, thus producing carbanions.

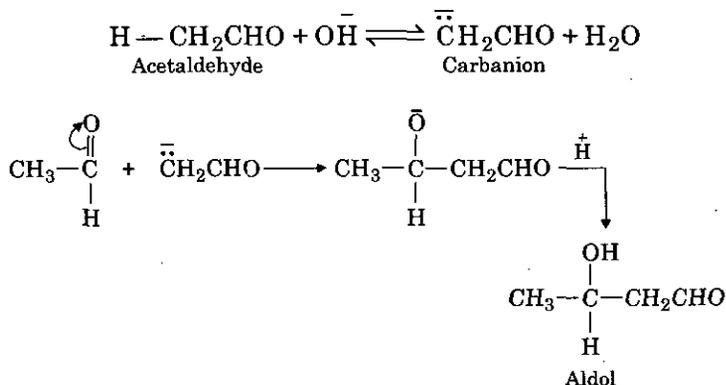


Carbanions are also formed by the decomposition of anions or addition of an anion to a double bond, e.g.,]



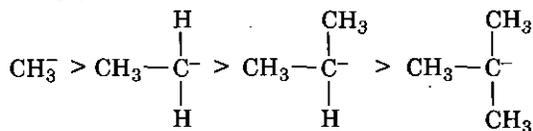
### Some Important Reactions Involving Carbanions

All the reactions of reactive methylene compounds such as malonic ester, toacetic ester etc., proceed via the formation of carbanions. Apart from these, aldol condensation reactions, base catalysed halogenation of ketones, addition reactions of Grignard's reagents proceed via the formation of carbanions.



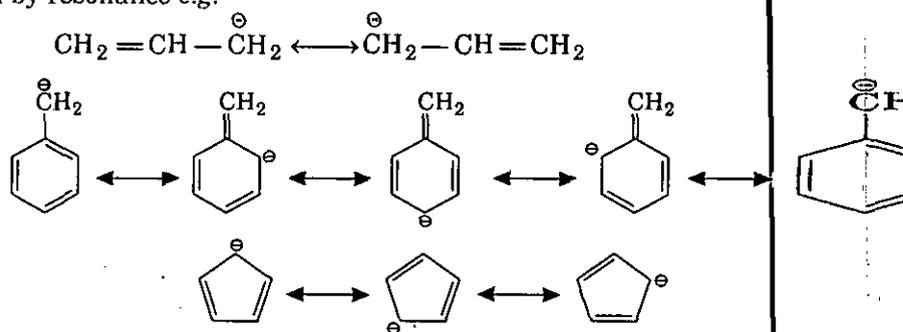
### Stability of Carbanions

Although carbanions are electron rich but they are very reactive and are easily attacked by electron deficient reagent (electrophiles). Ordinarily, carbanions are stable because of their negative charge. They are stabilized by the presence of an adjacent electron attracting group. The stability of carbanions is in the order,



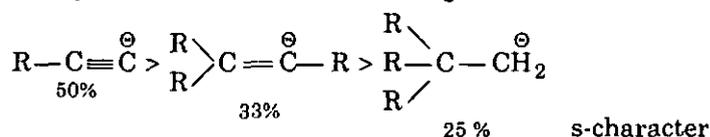
The stability of the carbanion may be explained by resonance and/or withdrawing substituents.

(a) **Resonance** : Stability of alkylic, benzylic and aromatic carbanion explained by resonance e.g.

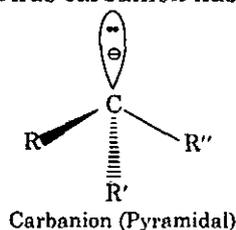


(b) **Resonance and -I effect** : When the carbanionic carbon is conjugated with a C=O or C≡N group the stability of the carbanion is greater than that of all benzyl type carbanion.

(c) **Contribution of s-character** : As the s-character in carbanionic increases stability of the carbanion increases e.g.



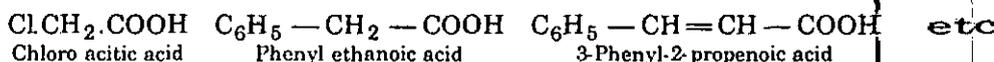
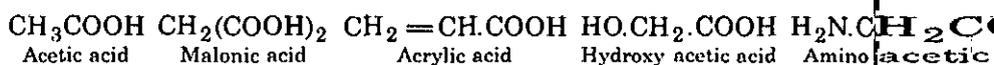
**Structure** : The carbanionic carbon atom shows  $sp^3$  hybridisation. Thus it has four hybrid orbitals which are tetrahedrally arranged. One of the hybrid orbitals possesses a lone pair of electrons. Thus carbanion has pyramidal structure.



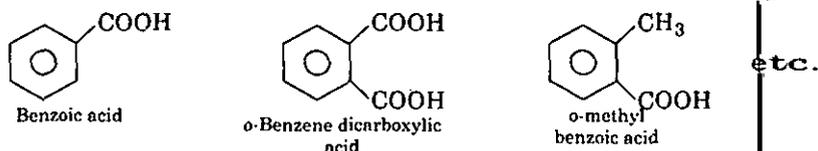
### • 3.8. STRENGTH OF ORGANIC ACIDS AND BASES

**Organic Acids** : The organic compounds in which one or more carboxylic groups (—COOH) is (are) present are known as organic acids. These are of two types.

(A) **Aliphatic carboxylic acids** : The general formula of such acids is  $\text{R}-\text{COOH}$  where R is aliphatic residue. The R may be saturated or unsaturated and substituted or unsubstituted e.g.



(B) **Aromatic carboxylic acids** : In such acids one or more —COOH groups (are) directly attached to the aromatic nucleus i.e., nuclear substitution e.g.



These compounds form salt with bases, therefore they show acidic character.

The acidic strength (character) of the acid depends upon its dissociation in a medium. It may be represented as :



$$K = \frac{[\text{RCOO}^-][\text{H}_3\text{O}^+]}{[\text{R.COOH}][\text{H}_2\text{O}]}$$

$$K_a = \frac{[\text{RCOO}^-][\text{H}_3\text{O}^+]}{[\text{RCOOH}]}$$

where  $K_a$  is ionisation constant of acid,  $\text{RCOOH}$ .

Evidently  $K_a$  is directly proportional to the concentrations of ionised entities; while inversely proportional to the concentration of unionised entity. As the value of  $[\text{H}_3\text{O}^+]$  or  $[\text{H}^+]$  increases the value of  $K_a$  increases *i.e.*, acidic strength of the acid increases. Thus  $K_a$  is a true index of the acidity or acidic strength (character) of the acid. But acidic strength is expressed as  $pK_a$ . The terms  $K_a$  and  $pK_a$  are related as:

$$pK_a = -\log K_a$$

Let us calculate the  $pK_a$  value for acetic acid. ( $K_a = 1.85 \times 10^{-5}$ ).

$$\begin{aligned} pK_a &= -\log (1.8 \times 10^{-5}) \\ &= -\log 1.8 - \log 10^{-5} \\ &= -0.26 + 5 = 4.74 \end{aligned}$$

Obviously, the  $pK_a$  value for strong acid would have small value whereas weak acid would have higher value than acetic acid. In other words **stronger acid has smaller  $pK_a$  value** (*i.e.*, larger  $K_a$  value).

The acidic strength of the acid changes by substitution in the acid. Acid strength of the acid increases by the substitution of electron withdrawing group (*i.e.*, -I effect) and decreases by the substitution of electron releasing group (*i.e.* +I effect). The  $pK_a$  values of some aliphatic acids are presented in the table.

#### $pK_a$ Values of Some Aliphatic Acids

Acid	$pK_a$	Acid	$pK_a$
HCOOH	3.6	Cl.CH <sub>2</sub> COOH	3.8
CH <sub>3</sub> COOH	4.7	Cl <sub>2</sub> .CH.COOH	1.3
CH <sub>3</sub> CH <sub>2</sub> COOH	4.8	Cl <sub>3</sub> .C.COOH	0.6
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> COOH	4.8	CH <sub>3</sub> .CH(Cl)CH <sub>2</sub> COOH	4.1
CH <sub>3</sub> .CH <sub>2</sub> .CH(Cl)COOH	3.8	Cl.CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> .COOH	4.5

Similarly different substituents effect the acidic character of benzoic acid ( $pK_a = 4.2$ ). The ortho derivatives are more acidic than meta and para derivatives, it is due to **ortho-effect**. Hydroxy (-OH) and methoxy (-OCH<sub>3</sub>) substituents show anomalous behaviour because highly electronegative element (oxygen) is directly attached in the benzene ring.  $pK_a$  values of different substituted benzoic acids are present in the following table.

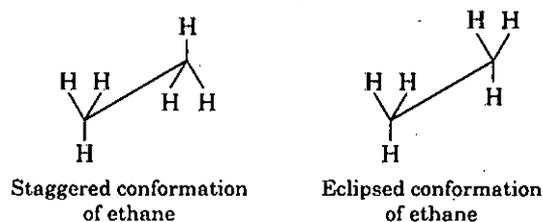
#### $pK_a$ Values of Substituted Benzoic Acid [ $pK_a$ value of Benzoic acid = 4.2]

Substituent	$pK_a$ Value		
	ortho	meta	para
CH <sub>3</sub>	3.9	4.3	4.4
OCH <sub>3</sub>	4.1	4.1	4.5
OH	3.0	4.1	4.6
Cl	2.9	3.8	4.0
NO <sub>2</sub>	2.2	3.4	3.5

carbon-carbon bond. The carbon atom towards the front is represented by a dot and the carbon atom towards the rear by a circle. The atoms or groups attached to the carbon are depicted as being bonded to the dot or circle.

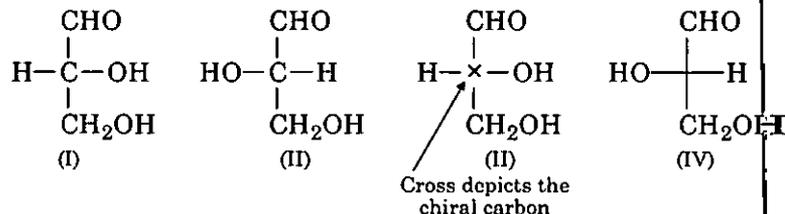
### [II] Sawhorse Projection Formula

The sawhorse formula represents the spatial arrangement of all the atoms on two adjacent carbon atoms. The bond between the adjacent carbon atoms is shown as a diagonal line usually from lower left to upper right, the left hand bottom end of the line represents the atom nearest to the observer and the right hand top end, the atom furthest away. Two of the remaining bonds to the two atoms are drawn vertically and the other two at 120° angles to these two as shown in figure.



### [III] Fischer Plain Projection Formula

In this projection, all bonds are drawn as solid lines with the underlined horizontal bonds (both left and right) pointing towards the observer (above the plane of the paper) and vertical bonds pointing away from the observer (below the plane of the paper). The chiral carbon atom lies in the plane of the paper and usually it is omitted, e.g. Fischer projections of the two forms of glyceraldehyde are represented by (I) and (II) and (III) and (IV).



If Fischer projections are to be used then certain following rules must be obeyed. Certain conventions understood, otherwise the structure will be misinterpreted.

- (i) The carbon chain of the molecule is arranged vertically, with the most oxidized carbon at the top or put the carbon number 1 at the top.
- (ii) The asymmetric carbon atom is put at the intersection of the crossed lines.
- (iii) The groups attached to the vertical lines are understood to be going back behind the plane of the paper, *i.e.*, the vertical lines represent bonds going away from the observer.
- (iv) The groups attached to the horizontal lines are understood to be coming forward out of the plane of the paper, *i.e.*, the horizontal lines represent bonds coming towards the observer.

### [IV] Flying Wedge Projection Formula

This is the most commonly used model. In this projection formula three types of lines are used in a standard way to show three dimensional structures in a two dimensional picture. A solid wedge (▴, thick lines) depicts a bond projecting above the plane of the paper towards the observer. Continuous lines (—, solid line) are bonds in the plane of the paper. A broken wedge (▬, dashed lines) depicts a bond in the plane of the paper, *i.e.*, a bond pointing away from the observer.



Flying-wedge representation of the two forms of glyceraldehyde.

### Differences between conformation and configuration.

Configuration	Conformation
1. The configuration of a molecule is the spatial arrangement of atoms and groups about a rigid part of the molecule <i>i.e.</i> , about a double bond or ring and about a dissymmetric part of the molecule.	1. The conformations of a molecule are the different spatial arrangements of its atoms and groups that arise due to the rotation of a part of the molecule about a single bond.
2. Configurations are not easily interconvertible.	2. Conformations are easily interconvertible, they get converted even at room temperature.
3. A molecule can have only one configuration <i>i.e.</i> , a different configuration will give different molecule.	3. A molecule could have an infinite number of conformations.
4. The difference of energy between two configurations is more than 84 kJ mole <sup>-1</sup> .	4. Conformations have low energy barriers, which varies from 4.2 to 46 kJ mole <sup>-1</sup> .
5. Interconversions of configurations involve bond breaking and bond forming processes.	5. Interconversions of conformation involve rotation of part of a molecule about a single bond.

### 3.12. CHIRALITY

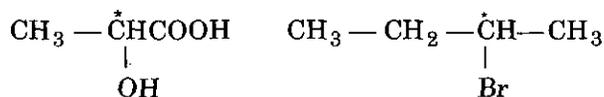
The term chiral (*Greek* : cheir = hand) was first coined by Kelvin (1884) for those substances which have 'handedness' *i.e.*, object and mirror image relationship of a left and right hand.

Those molecules which are not superimposable on their mirror images are called **chiral** molecules and are said to possess **chirality**. Chirality (non-superimposability on mirror image) is the main criterion for showing optical activity as well as enantiomerism. Enantiomerism is exhibited by compounds only when their molecules are chiral. If a molecule or object is superimposable on its mirror image, it is **achiral** (**non-chiral**). Achiral molecules are optically inactive and do not exhibit enantiomerism.

The terms chiral and chirality are now widely accepted and they have replaced the earlier terms, *viz.*, asymmetric asymmetry, dissymmetric and dissymmetry.

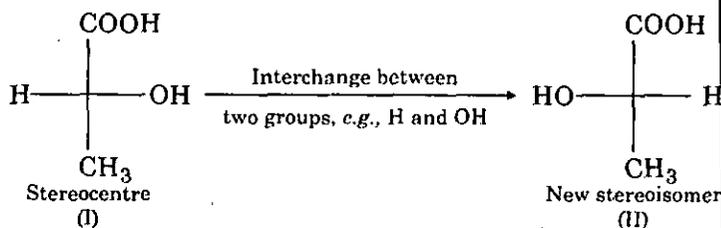
#### Stereogenic Centre

A carbon bonded to four different groups or atoms is known as a **chiral centre**. The term **chirality centre** is the most recently IUPAC approved term for the earlier used terms like chiral centre, chiral carbon or an asymmetric carbon. The chirality centre is indicated by an asterisk in each of the following compounds.

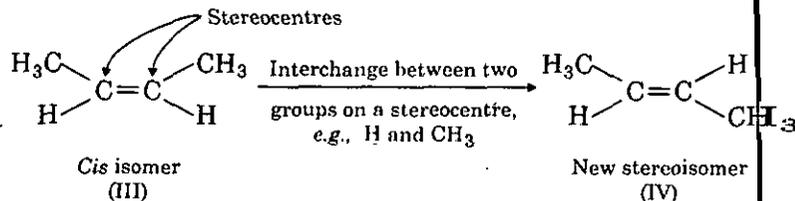


A stereogenic centre (stereocentre) is defined as an atom on which an interchange of any two atoms or groups results in a new stereoisomer. If the new stereoisomer is an

enantiomer, the stereocentre is called *chiral centre*. All stereocentres are tetrahedral.



Stereocentres I and II are enantiomers, so the stereocentre is a *chiral centre*.

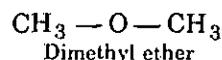
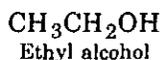


Stereocentres III and IV are not enantiomers. They are diastereomers, so in this case, stereocentres are not chiral centres. Moreover, they are not tetrahedral. Thus, we can say that *all chiral centres are stereocentres, but all stereocentres are not chiral centres*.

A molecule which contains only one chiral centre, must be chiral. Molecules which contain two or more chiral centres may or may not be chiral, e.g., *meso-tartaric acid* contains two chiral centres, but it is achiral. Many but not all chiral molecules contain chiral centres, e.g., many biphenyl derivatives are chiral but do not possess any chiral centres. Therefore, the absence or presence of a chiral centre is no criterion of chirality. The ultimate and final test for chirality is that a molecule or object cannot be superimposed on its mirror image.

### • 3.13. ISOMERISM

Compounds which have the same molecular formula but different physical or chemical properties are called *isomers* and this phenomenon is known as *isomerism*. For example, molecular formula  $\text{C}_2\text{H}_6\text{O}$  can represent the following organic compounds :



Both the compounds contain the same number of carbon, hydrogen and oxygen atoms. However, the difference in their properties must be also due to the difference in the relative arrangement of atoms in the compounds. Broadly speaking isomerism is of two types :

(i) **Structural isomerism** : When the isomerism is due to the difference in the relative arrangement of atoms within the molecule without any reference to space, this phenomenon is known as *structural isomerism*.

(ii) **Space isomerism or stereo-isomerism** : This isomerism is due to the different arrangement of atoms or groups in space. In other words, stereoisomers have the same structural formulae but have different configurations. It is of two types: (A) Geometrical isomerism and (B) Optical isomerism. Both these are described here.

#### [A] Geometrical Isomerism

The two carbon atoms can easily be rotated if attached by a single bond e.g., ethane, propane etc. But they can not rotate if attached by a double bond and the fixed union of two tetrahedra at two common corners gives different arrangements of atoms or groups in space provided they are different on each carbon atom. Thus,  $\text{C}_2\text{a}_2\text{b}_2$  can be represented as :

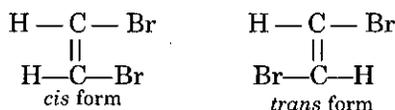


The isomerism which arises due to the different geometrical arrangements of atoms or groups about doubly bonded carbon atom is known as **geometrical isomerism** and the isomers are called as **geometrical isomers**. The isomer in which same or similar groups lie on the same side is called as **cis isomer** (Latin, *cis* = same side) and the isomer in which same or similar groups lie on the opposite sides in space is called as **trans isomer** (Latin, *trans* = across) and the phenomenon is also called as **cis trans isomerism**.

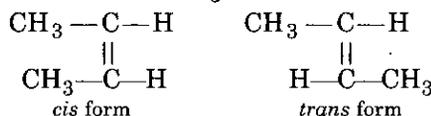
In general, all alkene compounds having the general formula  $abC = Cxy$  or a more simple formula  $abC = Cab$  show the phenomenon of geometrical isomerism. On the other hand, the compounds of the general formula,  $abC = Cxx$  will not show geometrical isomerism as one of the carbon atom contains same atoms or groups. Some examples are as follows :

Examples :

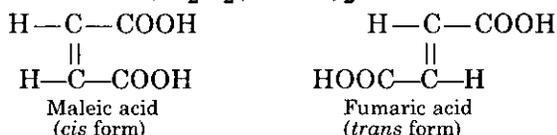
(1) 1, 2-Dibromoethene,  $\begin{array}{c} \text{CHBr} \\ || \\ \text{CHBr} \end{array}$



(2) Butene-2,  $\text{CH}_3 - \text{CH} = \text{CH} - \text{CH}_3$



(3) Maleic and fumaric acids,  $\text{C}_2\text{H}_2(\text{COOH})_2$



### Geometrical Isomerism of Oximes or $>C=N$ Compounds

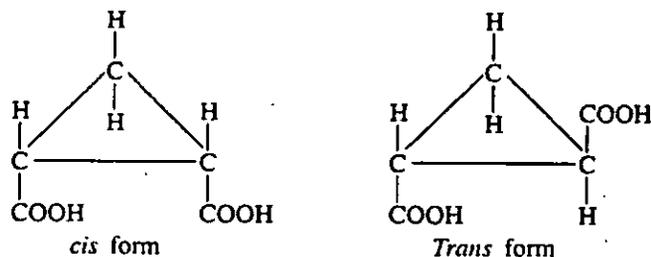
The carbon and a nitrogen atom joined by a double bond ( $>C=N$ ) can not easily rotate similar to two carbon atoms joined by a double bond ( $>C=C<$ ). The positions of various groups attached to  $>C=N$  are fixed in space and such compounds, therefore, show geometrical isomerism. The geometrical isomers of benzaldoxime may be represented as :



The isomer in which H and OH groups are on the same side is known as **cis** or **syn**, while the isomer in which H and OH groups are on opposite sides is known as **anti** or **trans** form.

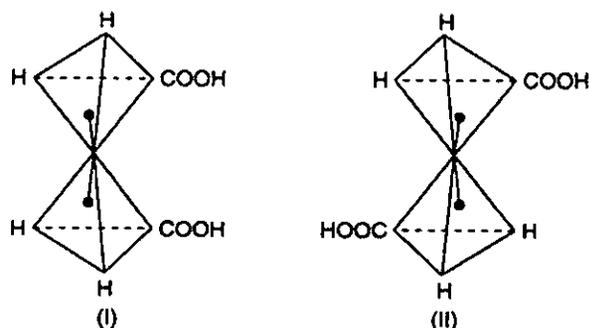
### Geometrical isomerism of Alicyclic or Ring compounds

Geometrical isomerism is also shown by ring compounds. In the ring compounds there is no free rotation around  $C-C$  single bonds as the rotation will break the bonds as well as the ring. For example, geometrical isomers of cyclopropane dicarboxylic acid may be represented as :



### Explanation of Geometrical Isomerism

According to van't Hoff and Le Bel, the four valencies of carbon atom are directed towards four corners of a regular tetrahedron, at the centre of which carbon atom is situated. The angle between any two valency bonds is  $109^{\circ}28'$ . According to this theory, a compound containing two carbon atoms united by a single bond can be represented by two tetrahedra joined together corner to corner as given below for succinic acid :

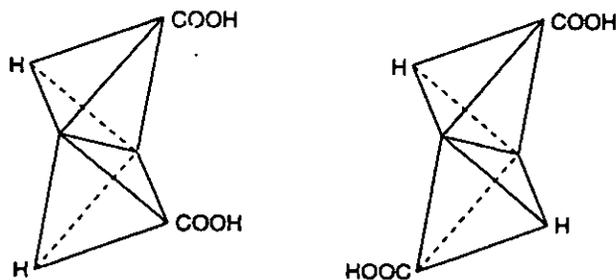


Identical molecules of succinic acid.

If two tetrahedra were fixed rigidly to each other, the two compounds having the models I and II should be possible. In fact, there is only one succinic acid known. Therefore, it is concluded that there occurs a free rotation of carbon atoms about the single bond and there is no possibility of two space models in such cases.

If the two carbon atoms are joined by a double bond, the two tetrahedra representing them must be in contact at two common corners and their free rotation ceases. Therefore, in such compounds, the position of the groups attached to two carbon atoms are fixed relative to each other.

Thus, different geometrical arrangements of groups about the doubly bonded carbon atom now become possible. For example, tetrahedral models of maleic and fumaric acid may be represented as :



Tetrahedral models of maleic and fumaric acids.

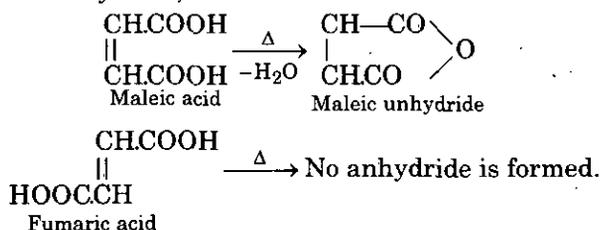
The lack of free rotation by doubly bonded carbon atoms or carbon and nitrogen atoms forms the basis of geometrical isomerism. It is confirmed by the fact that when maleic and fumaric acids are reduced to succinic acid, the isomerism disappears due to the free rotation of carbon-carbon single bond.

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### Determination of Configuration of Isomers

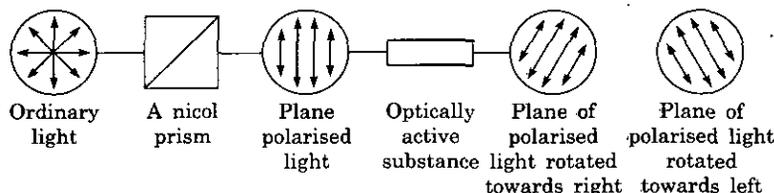
(i) **By Physical methods :** In general, it has been observed that the *cis* isomer has a lower melting point, a higher boiling point, a greater solubility in organic solvent, a higher density, a higher dipole moment, a higher heat of combustion and a higher ionization constant as an acid. The modern analytical techniques like X-ray analysis, infrared, ultraviolet and Raman spectra have also been used for this purpose.

(ii) **By formation of a cyclic compound** : The formation of a cyclic compound takes place easily when the two reacting groups are close to each other. Maleic acid readily form cyclic anhydride, whereas fumaric acid does not



### [III] Optical Isomerism

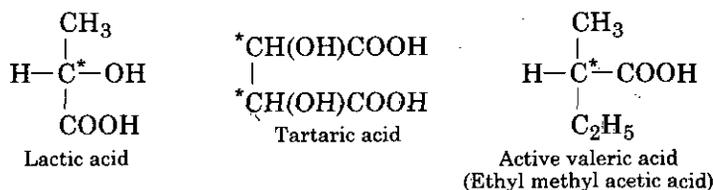
An ordinary ray of light vibrates in all directions perpendicular to its path of propagation. When it is passed through a nicol prism, the emerging rays vibrate only in one plane and the plane along which vibrations occur is known as plane of polarisation. **The substances which rotate the plane of polarised light are said to be optically active and this property is known as optical activity.**



Polarization of light

Isomers which have similar physical and chemical properties but differ in their behaviour towards polarised light are called **optical isomers** and the phenomenon is known as **optical isomerism**. The isomer which rotates the plane of polarised light in clockwise direction is known as **dextrorotatory or d-form or (+) form**. The isomer which rotates the plane of polarised light in anti-clockwise direction is known as **laevo-rotatory or l-form or (-) form**. The isomer which does not rotate the plane of polarised light in any direction is known as **optically inactive**. The *d*- and *l*-forms of a compound are always related to each other as object to image and are called as **enantiomorphs, enantiomers** or **antimers**.

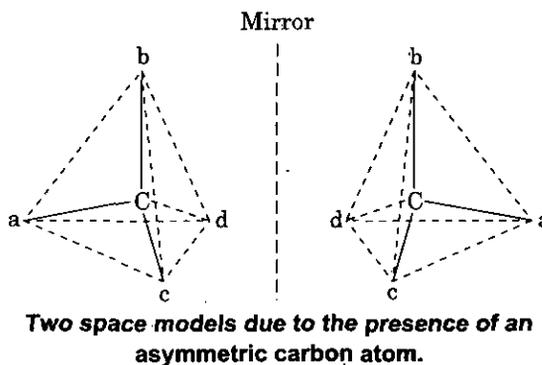
For a compound to show optical activity, it must contain an asymmetric (chiral or stereogenic) carbon atom, *i.e.*, a carbon atom which is attached with four different atoms or groups. For example, lactic acid, tartaric acid, active valeric acid, amyl alcohol etc.



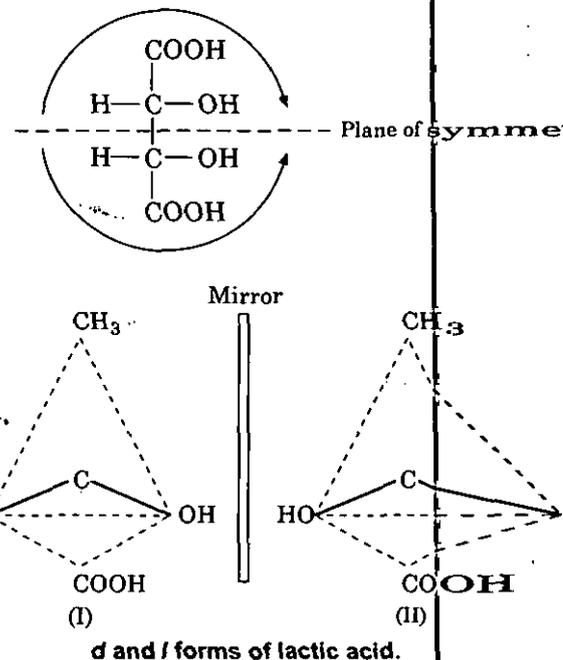
According to van't Hoff, the number of optical isomers is given by  $2^n$ , where  $n$  is the number of dissimilar asymmetric carbon atoms.

#### Explanation of Optical Activity :

According to van't Hoff and Le Bel, the four valencies of the carbon are directed towards four corners of a regular tetrahedron, at the centre of which carbon atom is situated. The angle between any two valency bonds is  $109^\circ 28'$ . If four different atoms or groups are attached to such a carbon atom, then the following two arrangements are possible.



These two arrangements are not super-imposable and show mirror image relationship. Such molecules are called as chiral and this property is known as molecular chirality. Hence, the compounds containing an asymmetric or chiral carbon atom are capable of showing the phenomenon of optical isomerism. On the other hand, there are certain compounds which contain two or more asymmetric carbon atoms and yet they are optically inactive. It means that the presence of asymmetric carbon atom is not only sufficient to make the molecule optically active. Actually, the molecule as a whole should be asymmetric. **Thus, molecular asymmetry or chirality is an essential condition for the compound to show optical activity.** If the molecule contains a plane of symmetry or centre of symmetry, the molecule becomes optically inactive due to internal compensation.



A plane of symmetry is an imaginary plane which divides the molecule into two parts such that each part is the mirror image of the other. The molecules having such plane are always optically inactive due to internal compensation.

A centre of symmetry is an imaginary point in the molecule such that if a line drawn from any group of the molecule to this point and then extending the line to an equal distance beyond the point, it meets the mirror image of the original group. For example, trans-dimethyl diketo piperazine contains centre of symmetry and is optically inactive.

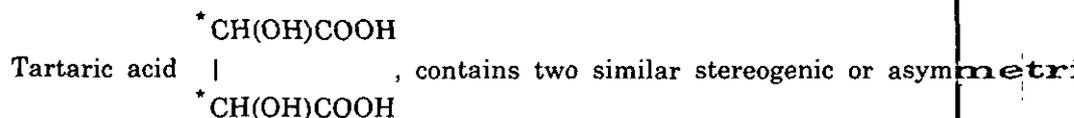
**(i) Optical Isomerism of a Compound Containing One Stereogenic (Asymmetric) Carbon Atom :** The most common example of a compound containing one stereogenic carbon is lactic acid,  $\text{CH}_3 \cdot \text{CH}(\text{OH})\text{COOH}$ . It contains one asymmetric carbon atom and according to van't Hoff it can exist in the following two optically active forms which are related to each other as object to image. The priority order of rotating the plane of polarised light of four groups attached to an asymmetric carbon atom in lactic acid is  $-\text{OH} > -\text{COOH} > -\text{CH}_3 > -\text{H}$ . Therefore,

(a) Compound I will rotate the plane of polarised light in clockwise direction and is known as *d*-form.

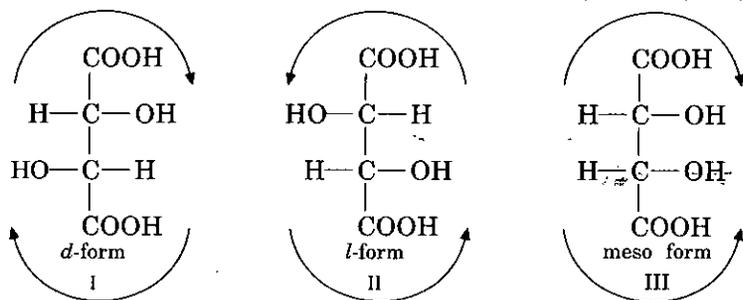
(b) Compound II will rotate the plane of polarised light in anticlockwise direction and is known as *l*-form.

(c) A third form results when equal amounts of *d*- and *l*-forms are mixed together. It is called as *racemic* form or *dl* mixture. It is optically inactive due to external compensation.

**(ii) Optical Isomerism of a Compound Containing Two Similar Stereogenic Carbon Atoms :** The most common example of a compound containing two similar stereogenic (asymmetric) carbon atom is tartaric acid.



carbon atoms, each of which is attached to four different groups, i.e.,  $-\text{H}$ ,  $-\text{OH}$ ,  $-\text{COOH}$ ,  $-\text{CH}(\text{OH})\text{COOH}$ . Due to the presence of two similar asymmetric carbon atoms, the configurations of various groups in tartaric acid can be represented in the following three ways :



(a) Compound I will rotate the plane of polarised light in clockwise direction and is known as *d*-form.

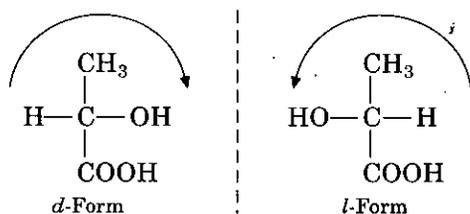
(b) Compound II will rotate the plane of polarised light in anti-clockwise direction and is known as *l*-form.

(c) Compound III will not rotate the plane of polarised light in any direction and is known as *meso* form. It is optically inactive due to internal compensation. The half of the molecule rotates the plane of polarised light in clockwise direction, whereas the remaining half equally rotates the plane of polarised light in anti-clockwise direction.

(d) A fourth form results when equal amounts of *d* and *l*-forms are mixed together. It is called as *racemic form* or *dl* mixture. It is optically inactive due to external compensation. The *d*-form rotates the plane of polarised light in clockwise direction and its rotation is balanced by an equal but opposite rotation of *l*-form.

### Enantiomers

Enantiomers or enantiomorphs or antimers are the *d*- and *l*-forms of an optically active compound which are related to each other as object to image. By the *d*-form means dextrorotatory, (*D*-) *i.e.*, which rotates the plane of polarised light in clockwise direction and *l*-form (*L*-) means laevorotatory, *i.e.*, which rotates the plane of polarised light in anti-clockwise direction.



### Properties of Enantiomers

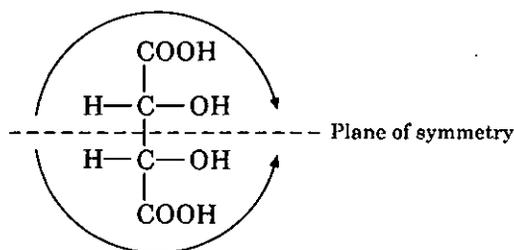
Enantiomers are stable compounds which differ from one another in three dimensional arrangements. They have same melting points, density, solubility, colour and reactivity. They differ only in their behaviour towards polarized light. The mixture of equal amounts of two enantiomers is called as racemic mixture. It is optically inactive.

### Racemic and Meso Forms

The compounds which contain one or more similar asymmetric carbon atoms but do not rotate the plane of polarised light are optically inactive. Such compounds are found in racemic and meso forms.

**Racemic form :** It is a mixture of equal amount of *d* - and *l* -forms. It is optically inactive due to external compensation. The *d* -form rotates the plane of polarised light in clockwise direction and its rotation is balanced by an equal but opposite rotation of *l* -form.

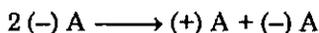
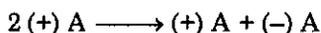
**Meso form :** It is only one compound containing two similar asymmetric carbon atoms. The compound is optically inactive as it contains plane of symmetry or centre of symmetry. The half of the molecule rotates the plane of polarised light in clockwise direction, whereas the remaining half equally rotates the plane of polarised light in



anti-clockwise direction. The molecule is, thus, optically inactive due to compensation. For example, one of the optical isomers of the tartaric acid is form.

### Racemisation

It has been observed that an optically active substance may be converted into an optically inactive racemic mixture under the influence of heat, light or some catalyst. For example, when a solution of *d*-tartaric acid is heated at 175°C, a racemic mixture of tartaric acid is obtained. *The conversion of a d- or l-isomer into its mirror image mixture is known as racemisation.* This involves the change of half of the active compound to the isomer of opposite rotation resulting in the racemic mixture.



Racemisation can be brought about in the following ways :

(i) **By heating** : Lactic acid, amyl alcohol, mandelic acid are racemised by heating.

(ii) **By heating with water** : *d*-tartaric acid is racemised by heating its aqueous solution at 175°C.

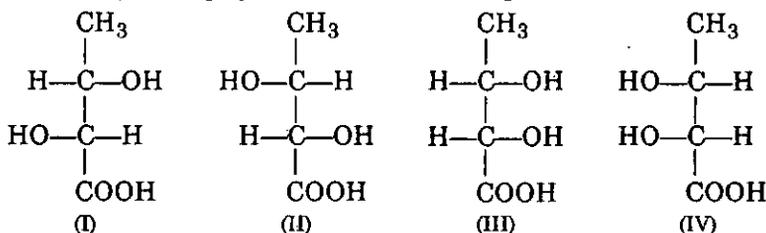
(iii) **By heating with dilute H<sub>2</sub>SO<sub>4</sub>** : *d*-Valeric acid is racemised by heating with dilute H<sub>2</sub>SO<sub>4</sub>.

(iv) **By heating with alkali** : Lactic acid, tartaric acid and mandelic acid are racemised by heating by the presence of alkali.

(v) **By auto racemisation** : In some cases, racemisation takes place itself in the presence of certain impurities. It is known as *auto racemisation*.

### Diastereoisomers or Diastereomers

The compounds which are optical isomers but not the mirror images are called **diastereo isomers** or **diastereomers**. For example, the compound, CH<sub>3</sub>CH(OH)CH(OH)COOH has two asymmetric carbon atoms and therefore, it can exist in the following four forms depending upon the relative arrangements of H and —OH groups.



The forms I and II are mirror images and so are the forms III and IV. The forms I and III, II and III, II and IV, I and IV although optically active but they are not the mirror images. These are called as **diastereoisomers**.

Diastereoisomers differ in their physical, chemical and optical properties. They can be separated by fractional distillation and by chromatographic techniques.

**Resolution**

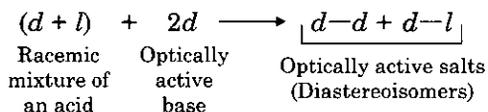
The separation of a racemic mixture (*dl* mixture) into *d*- and *l*-forms is known as **resolution**. When optically active compounds are prepared by synthetic methods, *d*- and *l*-forms are generally obtained in equal amounts. The racemic forms have identical physical properties and so they cannot be separated by ordinary methods such as fractional crystallisation or fractional distillation.

The following methods are used for resolution of a racemic mixture :

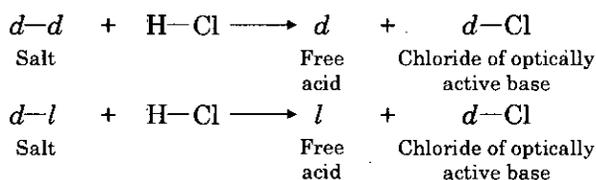
(i) **Mechanical separation** : This method is applicable for solid substances which form well defined crystals. The racemic mixture contains two types of crystals which have different shapes. They can be separated with the help of magnifying lens and a small force. This method is very difficult for practical purposes.

(ii) **Biochemical method** : This method was discovered by Pasteur in 1858. It is based on the fact that certain micro-organisms such as yeast, fungi or bacteria when allowed to grow in a solution of racemic mixture, destroy one of the optical isomers more rapidly than the other. For example, when *Penicillium glaucum* is allowed to grow in a solution of ammonium salt of racemic tartaric acid, *d*-form of ammonium tartarate is completely destroyed and *l*-form is left behind in solution. The method suffers from the defect that one optical isomer is obtained at the cost of the other.

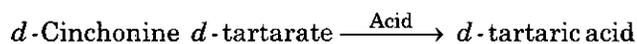
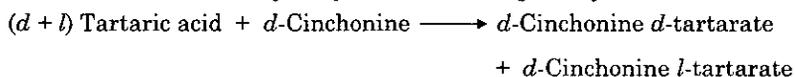
(iii) **Chemical or salt formation method** : This is the best method and is generally used for the resolution of acids and bases. Racemic acid is resolved with the help of optically active base and racemic base is resolved with the help of optically active acid. When a racemic acid is treated with optically active base, two types of salts known as diastereoisomers are obtained.



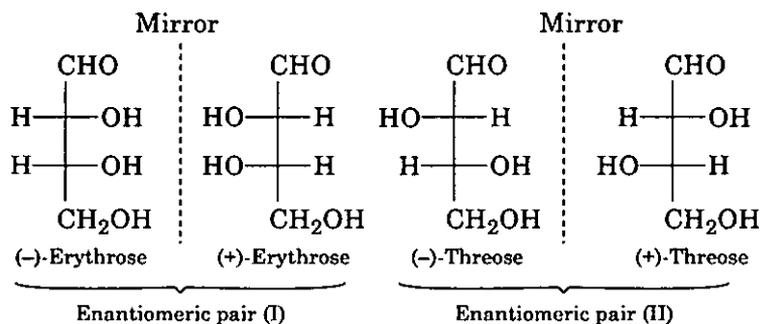
These salts have different solubilities and are separated by fractional crystallisation. They are then hydrolysed by dilute HCl to obtain original optically active isomers of the acid.



For example, when racemic tartaric acid is treated with *d*-cinchonine (base), two salts *d*-cinchonine *d*-tartarate and *d*-cinchonine *l*-tartarate are obtained. These salts are diastereoisomers and have different solubilities. They are separated by fractional crystallisation and then hydrolysed to obtain optically active tartaric acid.

**Threo and Erythro Diastereomers**

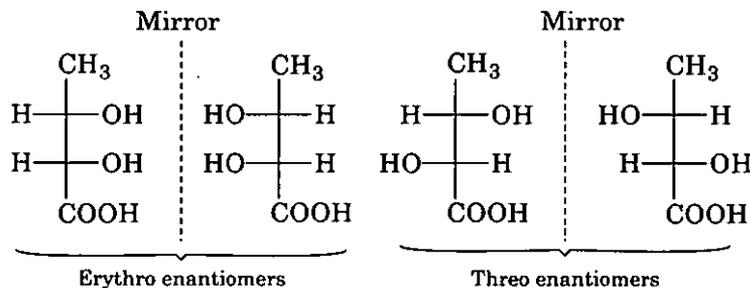
The compounds of the general formulae  $R-\overset{*}{C}ab-\overset{*}{C}ab-R'$  or  $R-\overset{*}{C}ab-\overset{*}{C}ac-R'$  are known as threo and erythro diastereomers. They possess two chiral carbon atoms. This nomenclature is based on aldotetroses, erythrose and threose, which exist as two enantiomeric pairs, we consider 2, 3, 4-trihydroxybutanal as :



Evidently one pair of enantiomer is the diastereomer with the other pair of enantiomer. The terms **erythro** and **threo** may be explained as :

The isomer in which two similar groups at two adjacent or non-identical chiral C-atoms are on the same side at the vertical line (in the Fischer projection) is known as erythro isomer and if the groups are on the opposite side is known as threo isomer.

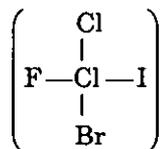
2, 3-Dihydroxybutanoic acid is other example of erythro and threo isomers, which may be shown as



### R, S System of Nomenclature of Optical Isomers

R, S system of configuration of optical isomers was given by Cahn, Ingold and Prelog (CIP). The symbols R and S are derived from the Latin words *rectus* means right and *sinister* meaning left. The configuration of an optically active compound is based upon the nature of the groups attached to an asymmetric centre. The nature of the group is determined by the priority of the groups which depends upon the following rules :

- (a) The four different atoms or groups attached to an asymmetric centre are arranged in the decreasing order of priority 1, 2, 3, 4.
- (b) When four different atoms are attached to an asymmetric centre, priority is given to atomic number. The atom with the highest atomic number is given the highest priority. Thus, in bromochlorofluoroiodo methane *i.e.*

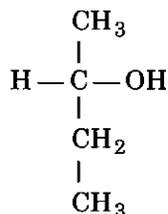


the priority sequence of four atoms is

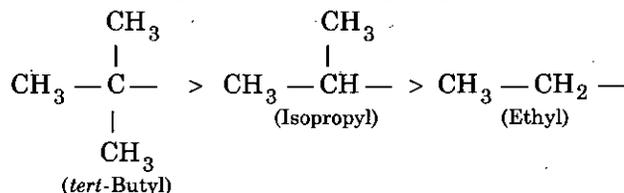
$$\text{I} (Z = 53), \text{Br} (Z = 35), \text{Cl} (Z = 17), \text{F} (Z = 9).$$

- (c) If isotopes of the same element are attached to an asymmetric centre, the isotope with higher mass number is given the higher priority. For example, deuterium ( ${}_1\text{H}^2$ ) is given higher priority as compared to hydrogen ( ${}_1\text{H}^1$ ).

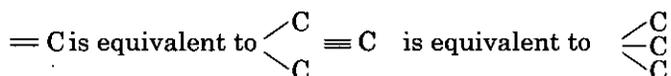
- (d) If two atoms attached to an asymmetric centre are same, the priority is determined by the atomic number of next atom away from asymmetric centre.



For example, in butanol-2, ethyl group has higher priority than methyl group because in ethyl group carbon atom is attached to C, H, H, whereas in methyl group carbon atom is attached to only hydrogen atom (H, H, H). Since carbon has higher atomic number than hydrogen, ethyl group has higher priority over methyl group. Similarly, the priority of *tert*-butyl-isopropyl and ethyl groups is in the order :

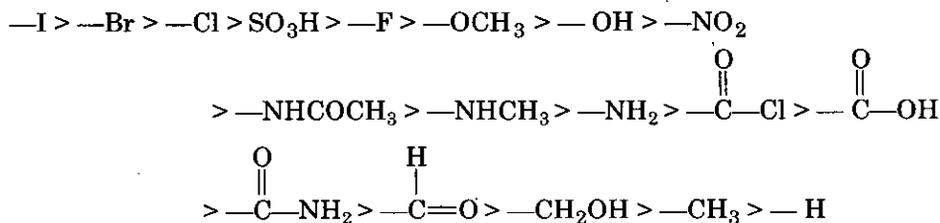


(e) An atom attached with a double or triple bond is equivalent to two or three such atoms. For example,



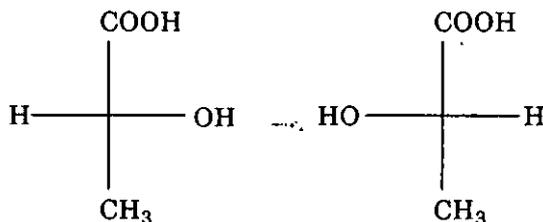
For example, out of  $-\text{CHO}$  and  $-\text{CH}_2\text{OH}$  groups,  $-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}=\text{O}$  group has higher priority than  $-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\text{OH}$  group. This is because in  $-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}=\text{O}$  group, C is attached to O, O, H atoms, whereas in  $-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\text{O}-\text{H}$ , C is attached to H, H and O. The third atom in  $-\text{CHO}$  is O (Z = 8), while in  $-\text{CH}_2\text{OH}$  it is H (Z = 1).

On the basis of these rules, some common groups are given the following priority sequence in the decreasing order :

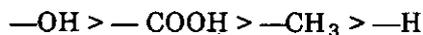


After giving priorities to four atoms or groups attached to an asymmetric centre, the molecule is now rotated so that the atom or group of lowest priority (4) is directed away from the viewer. Now the arrangement of remaining three atoms or groups is viewed in the decreasing order of their priorities. In looking so, if the eye moves in a clockwise direction, the configuration is assigned as R (*Rectus*, meaning right), while if the eye moves in anticlockwise direction, the configuration is assigned as S (*Sinister*, meaning left).

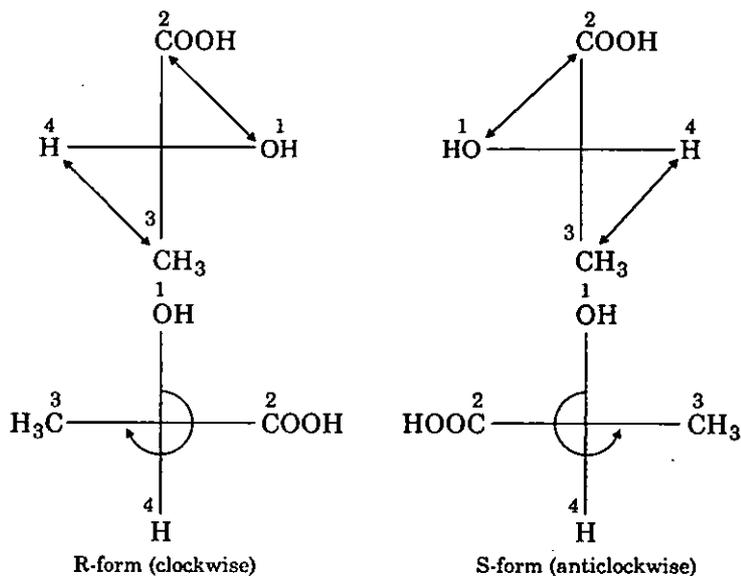
(a) R and S configurations of lactic acid,  $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$ : Lactic acid can be represented by the following projection formulae :



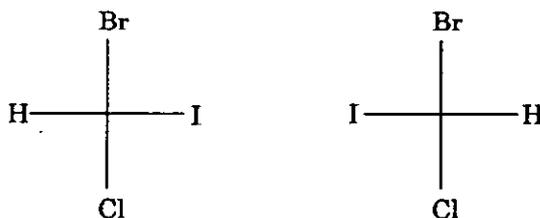
The priority order of four groups attached to an asymmetric carbon atom in lactic acid is,



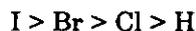
The interchange of two pairs of groups is done so as to keep the lowest priority H-atom below the vertical line. This will retain the original configuration. The interchange is represented by the double headed arrows in the following manner.



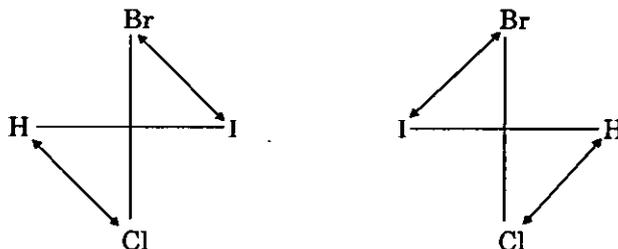
**(b) R and S configurations of bromo-chloro iodo-methane, CH(Cl)(Br)(I)**  
 The compound can be represented by the following projection formulae :

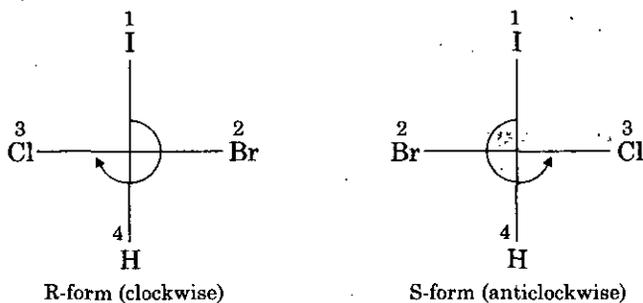


The priority order of four atoms attached to an asymmetric carbon atom in the above compound is

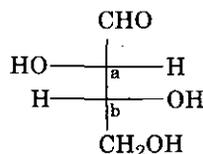


The interchange of two pairs of atoms is done so as to keep the lowest priority H-atom below the vertical line. This will retain the original configuration. The interchange is represented by the double headed arrows in the following manner :

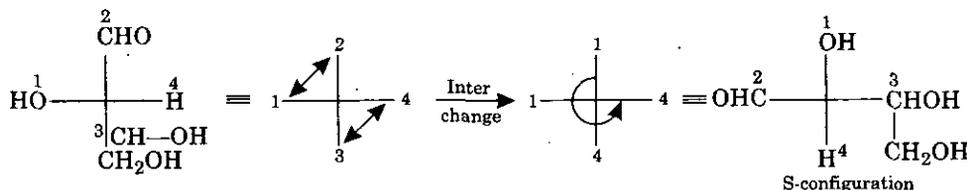




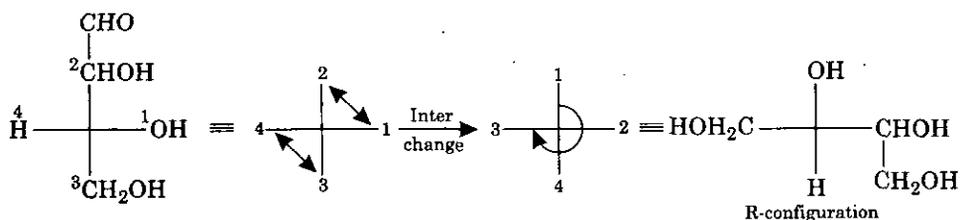
### (c) R and S configuration of



#### For chiral center 'a'



#### For chiral center 'b'



### E, Z System of Nomenclature of Geometrical Isomers

The configuration of geometrical isomers can be represented as cis or trans. When two identical atoms or groups are on the same side of the double bond, the isomer is known as cis (Latin, *cis* = same side) and if they are on the opposite side, it is called as trans (Latin, *trans* = across). When atoms or groups attached to doubly bonded carbon atom are different, cis trans designations cannot be applied. A new system of nomenclature of geometrical isomers (E and Z) has been introduced to name such stereo isomers. This system is based on a priority system developed by Cohn, Ingold and Prelog. The symbols E and Z have been taken from the German words *Entgegen* meaning opposite and *Zusammen* meaning together. The system of nomenclature involves the following steps :

(i) The atom or group of higher priority is determined on each doubly bonded carbon atom.



(ii) If the atoms or groups of higher priority (represented by A) on each carbon atom are on the same side of the double bond, the isomer is assigned the configuration, Z. On the other hand, if the atoms or groups of higher priority on each carbon atom are on opposite sides of double bond, the isomer is assigned the configuration, E.

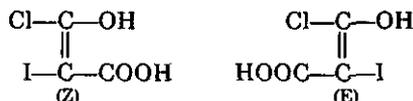


where A and B represent the atoms or groups of higher and lower priority, respectively.

(i) Consider an alkene in which doubly bonded carbon atoms are attached with the atoms F, Cl, Br and I as shown below :

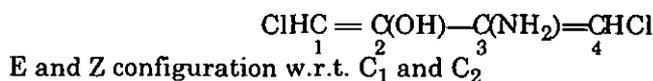
Now since I (Z = 53) has higher atomic number than F (Z = 9), it is given the highest priority. Similarly, bromine (Z = 35) has higher atomic number than chlorine (Z = 17). Thus, E and Z configurations of the isomers are assigned as above.

(ii) Consider an alkene in which doubly bonded carbon atoms are attached with —Cl, —OH, —COOH and I as shown below :

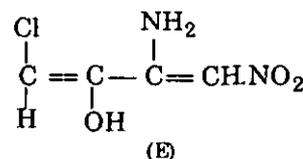
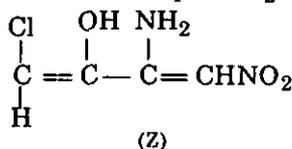


For the first carbon atom Cl has higher priority than —OH group and for the second carbon atom I has higher priority than —COOH. Thus, E and Z configurations of the isomers are assigned as above.

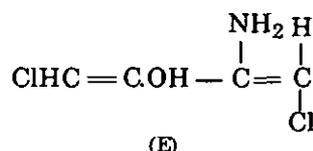
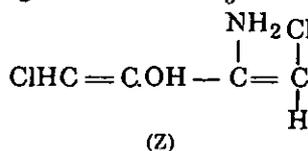
(iii) Consider a conjugated diene in which two double bonds (C=C) are present. In this case, we get two sets of E and Z configuration with respect to two C=C bonds. Let us consider following compounds :



E and Z configuration w.r.t. C<sub>1</sub> and C<sub>2</sub>



E and Z configuration w.r.t. C<sub>3</sub> and C<sub>4</sub>



### • SUMMARY

- The displacement of bond pair of electrons towards one direction is transmitted through the carbon atoms in a carbon chain is known as inductive (I) effect. It is a permanent effect.
- The displacement of electrons by electromeric effect is shown by bent arrow .
- Hyperconjugation is also known as σ-π conjugation.
- Reagents which show attraction towards electrons are called electrophilic reagents (or electrophiles) and those reagents which show attraction towards the nucleus are called nucleophilic reagents (or nucleophiles).
- Due to homolytic and heterolytic cleavage different reactive intermediates such as free radicals, carbocations, carbanions etc. are formed.
- Strength of acids and bases is effected by different types of substituents.
- Aromaticity of any hydrocarbon is decided by Huckel's rule i.e. (4n + 2)π electrons rule.
- The arrangements of atoms which can be changed into one another by rotation around single bonds are known as conformation.
- Those molecules which are not superimposable on their mirror images are called chiral molecules and are said to possess chirality.
- Compounds which have the same molecular formula but different physical and chemical properties are called isomers and the phenomenon is called isomerism.

- The isomerism which arises due to different geometrical arrangements of atoms or groups about doubly bonded carbon atoms is called geometrical isomers. The isomerism are called geometrical isomers e.g. maleic acid and fumaric acid.
- Isomers which have similar properties but differ in their behaviour towards polarised light are called optical isomers and the phenomenon is called optical isomerism.
- The *d*- and *l*-forms of an optically active compound which are related to each other as object to mirror image are called enantiomers.
- The compounds which are not optical isomers but not the mirror images are called diastereomers.

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• **STUDENT ACTIVITY**

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1. Write a note on inductive effect.

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2. State and explain electrophiles and nucleophiles with examples.

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3. What are reactive intermediates ? Discuss free radicals and carbocations.

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4. Discuss the strength of acids and bases.

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5. Describe conformation of cyclohexane.

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6. What are diastereomers and enantiomers.

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7. State and explain optical isomerism.

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8. Discuss CIP rules for R/S and E/Z configuration.

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• TEST YOURSELF

Answers the following questions :

1. Define inductive effect. How does it effect acidity of the acid and basicity of the base?
2. Explain electromeric effect.
3. Define electrophiles and nucleophiles with suitable examples.
4. Explain why chloroacetic acid is stronger than formic acid and acetic acid.
5. Explain why methyl amine is more basic than ammonia.
6. Mention the difference between an ion and free radical.
7. What do you know about homolytic and heterolytic fission ?
8. Write a short note on the following :  
(i) Carbocation (ii) Carbanion (iii) Free radical
9. What is Huckel's rule for aromaticity of a hydrocarbon ?
10. What do you know about (i) resonance and (ii) hyperconjugation ?
11. Explain the term conformation of cyclohexane.
12. Write the difference between conformation and configuration.
13. How do you represent three dimensional molecule on paper ?
14. What is chirality ?
15. Explain R, S system of configuration of optical isomers with a suitable example.
16. Explain, E, Z system of configuration of geometrical isomers with a suitable example.
17. What is optical isomerism ? Explain it by taking the examples of lactic acid and tartaric acid.
18. Write a short notes on the following :  
(i) Enantiomers (ii) Diastereomers
19. Which one of the following orders is correct regarding - I effect of the substituents  
(a)  $-NR_2 < -OR > -F$  (b)  $-NR_2 > -OR > -F$   
(c)  $-NR_2 < -OR < -F$  (d)  $-NR_2 > -OR > -F$
20. Which of the following acids is strongest :  
(a)  $CF_3COOH$  (b)  $CH_3COOH$   
(c)  $CCl_3COOH$  (d)  $CBr_3COOH$
21. According to Huckel's rule the number of  $\pi$ -electrons in any aromatic compound should be :  
(a)  $2n + 1$  (b)  $2n + 2$  (c)  $2n + 3$  (d)  $n + 4$
22. Which one is the correct order of the stability of the alkenes :  
(a)  $CH_2=CH_2 < CH_2=CH-CH_3 > CH_3-CH=CH-CH_3$   
(b)  $CH_2=CH_2 < CH_2=CH-CH_3 < CH_3-CH=CH-CH_3$   
(c)  $CH_2=CH_2 > CH_2=CH-CH_3 > CH_3-CH=CH-CH_3$   
(d)  $CH_2=CH_2 > CH_2=CH-CH_3 < CH_3-CH=CH-CH_3$
23. Indicate the wrong statement for resonance :  
(a) The energy of the resonance hybrids should be of same order.  
(b) The position of the atoms in resonance hybrid should be identical.  
(c) The number of unpaired electron in the resonance hybrid should be different.  
(d) All are correct
24. Which one of the following is a nucleophile :  
(a)  $SO_3$  (b)  $SO_2$  (c)  $C_2H_5OH$  (d)  $BCl_3$
25. Which one of the following is the product on homolytic cleavage of covalent bond  
(a) Free radical (b) Carbocation (c) Carbanion (d) Carbene
26. The shape of  $\overset{\ominus}{C}H_3$  ion is :  
(a) Triangular (b) Pyramidal  
(c) Tetrahedral (d) Octahedral

27. The most stable free radical is in the following :

- (a)  $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{CH}_2$  (b)  $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{CH}_3$   
 (c)  $\text{CH}_3\dot{\text{C}}\text{H}_2$  (d)  $\text{CH}_3\cdot\dot{\text{C}}\text{H}\cdot\text{CH}_3$

28. The number of optically active isomers of lactic acid and tartaric acid are, respectively.

- (a) 2, 4 (b) 2, 2 (c) 2, 3 (d) 3, 3

29. Which one of the following compounds show geometrical isomerism :

- (a)  $\text{ClCH}=\text{CHBr}$  (b)  $\text{CH}_2=\text{CHBr}$   
 (c)  $\text{Br}_2\text{C}=\text{CCl}_2$  (d)  $\text{CH}_2=\text{CHBr}$

30. Which one of the following groups has highest inductive effect :

- (a)  $\text{CH}_3$  (b)  $\text{C}_2\text{H}_5$  (c)  $(\text{CH}_3)_2\text{CH}$  (d)  $(\text{CH}_3)_3\text{C}$

31. Which one of the following compounds can occur in enantiomeric form

- (a)  $(\text{CH}_3)_2\text{CHCOOH}$  (b)  $\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}_3$   
 (c)  $\text{CH}_3-\underset{\text{NH}_2}{\text{CH}}-\text{CH}_3$  (d)  $\text{CH}_3-\underset{\text{NH}_2}{\text{CH}}-\text{CH}_2-\text{CH}_3$

32. Fill in the Blanks :

- (i) The shape of  $\dot{\text{C}}\text{H}_3$  ion is .....  
 (ii) The stability of ethene is ..... than that of 2-butene.  
 (iii) The basic strength of dimethylamine is ..... than that of ammonia.  
 (iv) Optically active isomers but not the mirror images are called as .....  
 (v) Isomers which can be inter converted by rotation around a single bond are .....  
 (vi) Butene-2 exists in ..... and ..... forms.

33. Identify True (T) and False (F) statements :

- (i) Electromeric effect is a permanent effect.  
 (ii) Resonance results in the stability of the molecule.  
 (iii) The inductive effect is symbolized as - I for the attraction of electrons.  
 (iv) The number of optically active isomers of tartaric acid are two.  
 (v) R, S system of nomenclature of configuration in geometrical isomers.  
 (vi) The number of conformation of ethane is infinite.

## ANSWERS

19. (c) 20. (a) 21. (b) 22. (b) 23. (c) 24. (c) 25. (a) 26. (b) 27. (b) 28. (c) 29. (a)  
 30. (d) 31. (d) 32. (i) Planar (ii) Less (iii) More (iv) Diastereomers (v) Conforms (vi) *cis, trans*  
 33. (i) F (ii) T (iii) T (iv) T (v) F (vi) T

CHEMISTRY OF ALIPHATIC HYDROCARBONS

STRUCTURE

- Alkanes
- Alkenes
- Alkynes
- Preparations of Alkanes, Alkenes and Alkynes
- Reactions of Alkanes, Alkenes and Alkynes
- Elimination and Addition Reactions and Mechanism
- Acidity of Alkanes, Alkenes and Alkynes
- Summary
- Student Activity
- Test Yourself
- Answers

LEARNING OBJECTIVES

After going this unit you will learn :

- Hydrocarbons, Longest chain rule, lowest sum rule and naming of side chain.
- Methods of preparation of alkanes and chemical properties of alkanes
- Reactivity and selectivity.
- Nomenclature alkenes and alkynes.
- Methods of preparation of alkenes; and chemical properties of alkenes.
- Methods of preparation of alkynes and chemical properties of alkynes.

CARBON-CARBON SIGMA BONDS

• 4.1. ALKANES

Organic compounds which contain only carbon and hydrogen are called as hydrocarbons. They contain two types of covalent bonds, carbon-carbon (C—C) and carbon-hydrogen (C—H). On the basis of structure, hydrocarbons may be open chain (acyclic) and closed chain (cyclic). Open chain hydrocarbons are further classified into two groups—saturated and unsaturated. The saturated hydrocarbons contain single covalent bonds between the carbon atoms, for example alkanes. Alkanes contain strong C—C and C—H covalent bonds. Therefore, this class of hydrocarbons are relatively chemically inert. Hence they are sometimes referred to as paraffins (Latin, parum affinis *i.e.* little affinity). The unsaturated hydrocarbons contain at least one double or triple covalent bonds between the carbon atoms. For example, alkenes (C=C) and alkynes (C≡C).

[I] IUPAC Nomenclature of Alkanes

Alkanes form a homologous series having the general formula  $C_nH_{2n+2}$ . The IUPAC name of a compound consists of two parts. The first part is prefix and second part is called as suffix. The prefix shows the longest possible chain of carbon atoms *e.g.*,

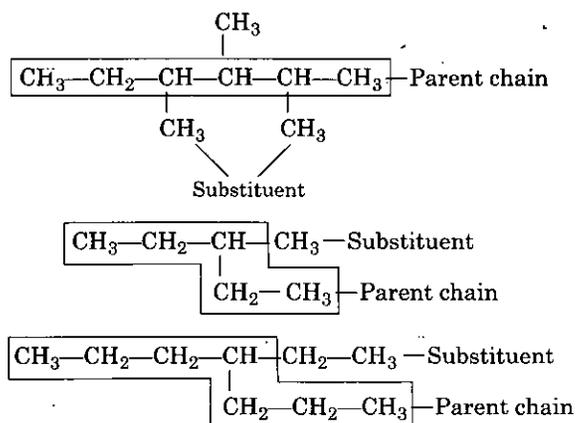
- |                         |                         |
|-------------------------|-------------------------|
| C <sub>1</sub> — Meth — | C <sub>5</sub> — Pent — |
| C <sub>2</sub> — Eth —  | C <sub>6</sub> — Hex —  |
| C <sub>3</sub> — Prop — | C <sub>7</sub> — Hept — |
| C <sub>4</sub> — But —  | C <sub>8</sub> — Oct —  |

The suffix shows the functional group and for each functional group, there is a separate suffix. The suffix of this class of compounds is 'ane'. Thus, IUPAC name of this class of compounds is alkane. The molecular formulae and names of some of the alkanes are given in the following table.

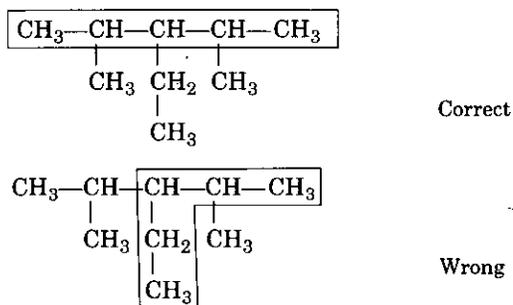
Molecular formula of the compound	Name of the compound
$\text{CH}_4$	Meth + ane = Methane
$\text{C}_2\text{H}_6$	Eth + ane = Ethane
$\text{C}_3\text{H}_8$	Prop + ane = Propane
$\text{C}_4\text{H}_{10}$	But + ane = Butane
$\text{C}_5\text{H}_{12}$	Pent + ane = Pentane
$\text{C}_6\text{H}_{14}$	Hex + ane = Hexane
$\text{C}_7\text{H}_{16}$	Hept + ane = Heptane
$\text{C}_8\text{H}_{18}$	Oct + ane = Octane

In addition, the following rules are used for the nomenclature of alkanes :

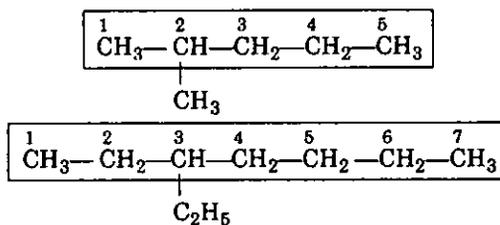
**(i) Longest chain rule :** *In the given compound, the longest continuous chain of carbon atoms is located and the compound is named as the derivative of that alkane.* The continuous chain may or may not be straight. The selected chain is called as parent or main chain and it gives the name of parent hydrocarbon. The carbon atoms which are not included in the parent chain are known as side chains or substituents.



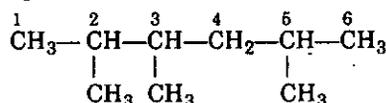
If two different chains of equal length are possible, the chain with maximum number of side chains is selected.



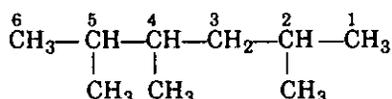
**(ii) Lowest number to the side chain and lowest sum rule :** *The carbon atoms of the chain are numbered from one end to the other by Arabic numbers. The numbering is done from the end which is nearest to the side chain. The positions of the side chains are indicated by the numbers given to the carbon atoms to which they are attached.*



When many substituents are present, the numbering is done from the end where upon the sum of substituent positions is minimum.



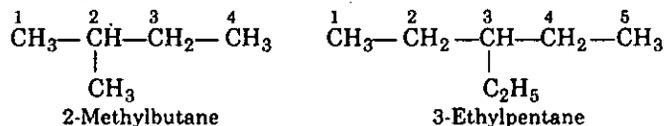
Sum of substituent positions = 2 + 3 + 5 = 10  
(Correct)



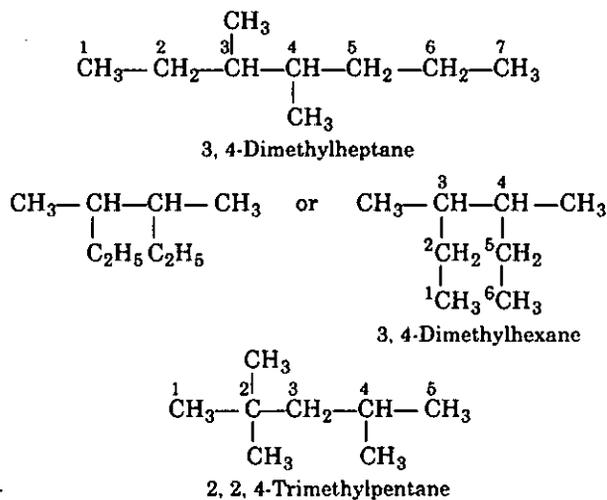
Sum of substituent positions = 2 + 4 + 5 = 11  
(Wrong)

### (iii) Naming of substituents or side chains

(a) When only one substituent is present in the compound : When only one substituent is present in the given compound, its name is prefixed to the name of parent alkane. The position of the substituent is also indicated by an appropriate number. The number is separated from the substituent by hyphen and no gap is left between the substituent and that of parent alkane.



(b) When same substituent is present more than once in the compound : When same substituent is present more than once in the compound, the prefix di, tri, tetra etc. are prefixed before the name of the substituent and their positions are written in increasing order separated by commas. For example,

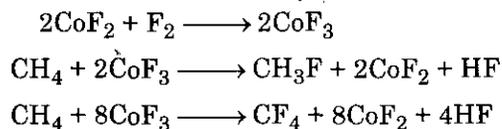


(c) When different substituents are present in the compound : When different substituents are present in the compound, they are named in the alphabetical order along with their appropriate positions.





Fluorination is an explosive reaction, due to that C—C and C—H bonds are broken. Although direct fluorination of alkanes is not useful, fluorine can be substituted for hydrogen *via* the use of less reactive fluorinating agents such as  $\text{CoF}_3$ .  $\text{CoF}_3$  as prepared by the reaction of  $\text{CoF}_2$  and  $\text{F}_2$ .



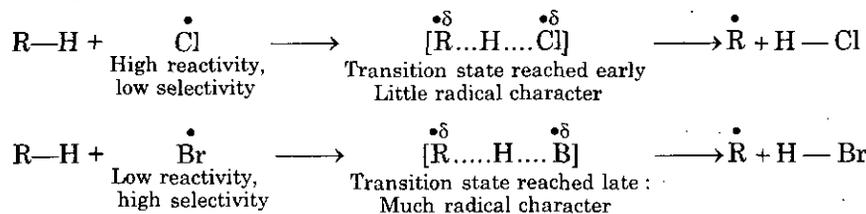
To explain about the facts  $\Delta H$  ( $\text{kJ mol}^{-1}$ ) values are presented in the following table in the formation of  $\text{CH}_3\text{X}$  in the four steps. Evidently in fluorination maximum amount of heat is liberated and iodination is an endothermic reaction.

$\Delta H$  ( $\text{kJ mol}^{-1}$ ) values for the Formation of  $\text{CH}_3\text{X}$

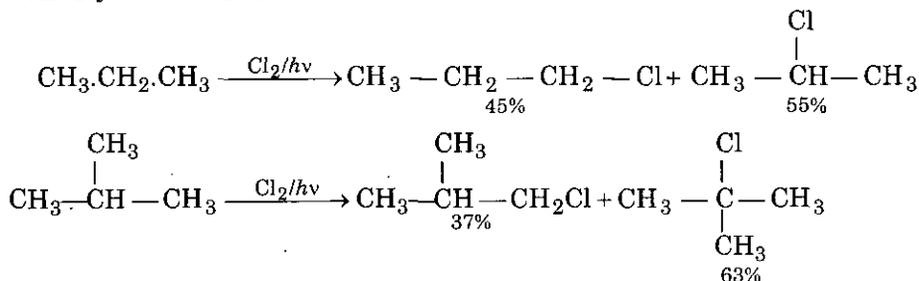
Reaction	F	Cl	Br	I
(i) $\text{X}_2 \longrightarrow 2\dot{\text{X}}$	+ 155	+ 244	+ 193	+ 152
(ii) $\text{CH}_4 + \dot{\text{X}} \longrightarrow \dot{\text{C}}\text{H}_3 + \text{HX}$	- 138	- 5	+ 63	+ 130
(iii) $\dot{\text{C}}\text{H}_3 + \text{X}_2 \longrightarrow \text{CH}_3\text{X} + \dot{\text{X}}$	- 298	- 96	- 88	- 71
(iv) $\dot{\text{X}} + \text{X}^\bullet \longrightarrow \text{X}_2$	- 155	- 244	- 193	- 152
$\Delta H$	- 436	- 101	- 25	+ 59

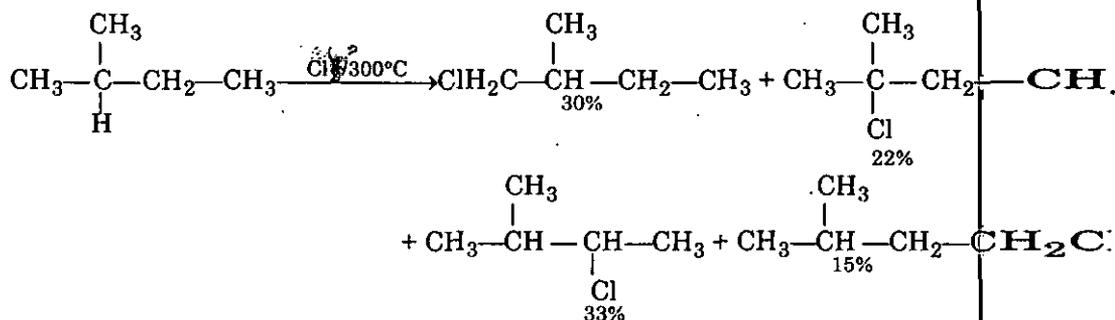
**Reactivity and Selectivity :** Regarding reactivity and selectivity, we state that, in the case of halogenation of alkanes. In the attack by a reagent of high reactivity, the transition state tends to resemble the reactants; while in the attack by a reagent of low reactivity, the transition state tends to resemble the product. A general relationship between reactivity and selectivity is that in a set of similar reactions, the less reactive the reagent, the more selective it is in its attack.

For example, the chlorination and bromination of alkane is considered here.



**Selectivity of chlorine :** A chlorine free radical ( $\text{Cl}$ ) is so reactive that it makes primary, secondary and tertiary radicals with almost equal ease. According to reactivity selectivity principle **the greater the reactivity of a species, less will be selectivity**. Chlorination reaction is not selective reaction.

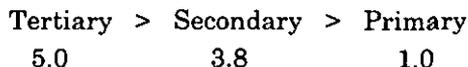




The ratios of products that we obtain from chlorination reaction of higher alkanes are not identical with what we would expect if all hydrogen atoms of the alkane were equally reactive.

After experimentally determining the amount of each of chlorination products obtained from various hydrocarbons, chemists were able to calculate that at room temperature it is 5.0 times easier for a chlorine radical to abstract hydrogen atom from a tertiary carbon than from a primary carbon, and it is 3.8 times easier to abstract hydrogen atom from secondary carbon than from a primary carbon. The precise ratio differs at different temperatures.

Thus relative rates of formation of alkyl radical by a chlorine radical is



To determine the relative amount of products obtained from radical chlorination of an alkane, for example *n*-butane, both the probability factor (the number of hydrogen atoms that can be abstracted that will lead to the formation of the particular product) and the reactivity factor (the relative rate at which a particular hydrogen is abstracted) must be taken into account.

(i) The relative amount of 1-chlorobutane

$$\begin{aligned} &= \text{Number of hydrogens present on } 1^\circ\text{-carbon} \times \text{reactivity factor} \\ &= 6 \times 1.0 = 6.0 \end{aligned}$$

(ii) The relative amount of 2-chlorobutane

$$\begin{aligned} &= \text{Number of hydrogens present on } 2^\circ\text{ carbon} \times \text{reactivity factor} \\ &= 4 \times 3.8 = 15.2 \end{aligned}$$

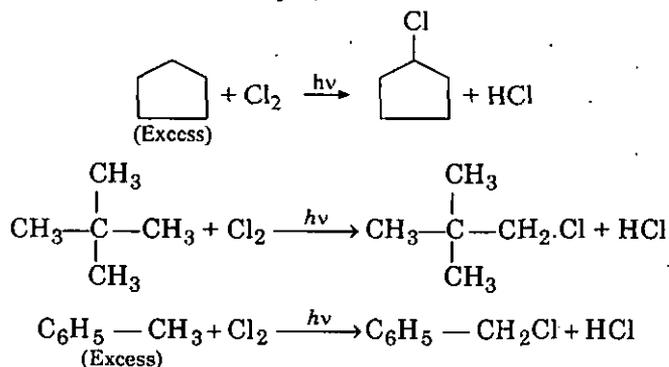
Sum of the relative amount of all products = 6 + 15 = 21

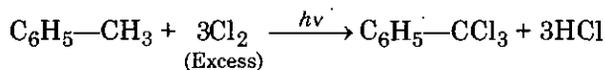
$$\text{Per cent yield} = \frac{\text{relative amount} \times 100}{\text{sum of relative amounts}}$$

$$\text{Thus per cent yield of 1-chlorobutane} = \frac{6 \times 100}{21} = 29\%$$

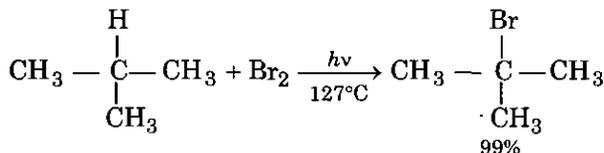
$$\text{Per cent yield of 2-chlorobutane} = \frac{15 \times 100}{21} = 71\%$$

Since chlorination is non-selective, it is a useful reaction only when there is one kind of hydrogen in the molecule. For example,





**Selectivity of Bromine :** Since bromine is less reactive than chlorine toward alkanes hence bromine is more selective in the site of attack when it does react. For example, when isobutane reacts with bromine almost whole the tertiary hydrogen atom replaces by bromine.



### CARBON-CARBON PI BONDS

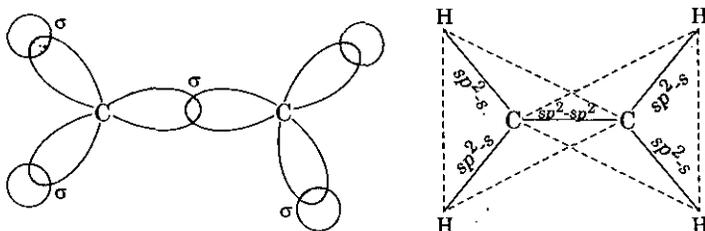
#### • 4.2. ALKENES

The unsaturated hydrocarbons which contain one carbon-carbon double bond, are called *olefins*. The name has emerged from olefiant (oil forming) as ethylene with chlorine forms an oily liquid, ethylene dichloride. This class has the general formula  $\text{C}_n\text{H}_{2n}$ . Ethylene,  $\text{CH}_2 = \text{CH}_2$  being the first member of this homologous series, the carbon-carbon double bond is, therefore, often referred to as ethylenic or olefinic double bond.

Each hydrocarbon of this homologous series has two hydrogen atoms less than the corresponding paraffin or alkane. The series is generally called as *alkylene* or *alkene* or *olefin* series.

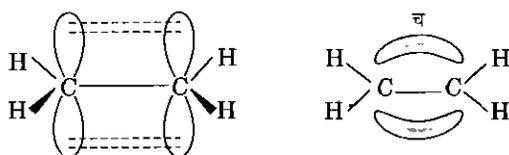
#### [I] Orbital Structures

A carbon atom bonding only with three other carbon atoms undertakes hybridisation of the  $s$  with the two  $p$ -orbital ( $p_x$  and  $p_y$ ). This type of hybridisation is known as  $sp^2$  hybridisation. This is trigonal, *i.e.*, forms an angle of  $120^\circ$  with each other. The unhybridised  $p_z$  orbital with its single electron remains as such as right angles to the hybridised orbital, *e.g.*, ethylene ( $\text{C}_2\text{H}_4$ ).



Orbital picture of ethylene depicting  $\sigma$ -bonds only.

One  $sp^2$  hybrid orbital of one carbon atom overlaps co-axially with that of another carbon atom to form a  $\sigma$ -MO (MO = molecular orbital) linking the two carbon atoms together. The remaining  $sp^2$  hybrid orbitals of two different carbon atoms form four  $\sigma$  (C—H) bonds. The six atoms of an ethylene molecule thus lie on the same plane, bond angles being  $120^\circ$ . The unhybridised  $2p_z$  orbitals of the two carbon atoms which are at right angles to the plane containing C and H atoms and are parallel to each other, overlap sideways to form  $\pi$ -MO. The  $\text{C} = \text{C}$  is thus a simple, graphical representation of one  $\sigma$  and one  $\pi$ -MO encompassing the two nuclei.



Orbital picture of ethylene depicting the formation of  $\pi$ -bond by the sideways overlapping of unused  $p$ -orbitals on each carbon.

The carbon-carbon single bonds in other alkenes are formed by the overlap of  $sp^3$  orbitals. The carbon-hydrogen bonds attached to carbon carrying the double bond are formed by the overlapping of  $sp^2$  and  $s$ -orbitals, while those attached to other carbons by the overlapping of  $sp^3$  and  $s$ -orbitals.

## [II] Nomenclature of Alkenes

There are two main systems of naming alkenes or olefins.

- (i) Trivial system and (ii) IUPAC system

(i) **Trivial system** : In this system, the olefins are named by replacing the suffix 'ane' of the corresponding paraffin with 'ylene', e.g.,  $C_2H_4$  is named *ethylene* after its corresponding paraffin, ethane ( $C_2H_6$ ). Similarly,  $C_3H_6$  as *propylene* after propane ( $C_3H_8$ ) and so on. In general, therefore, alkenes are called 'alkylenes' from 'alkanes'.

(ii) **IUPAC system** : In this system, they are named after the corresponding alkane by changing the suffix 'ane' into 'ene', hence in general, they are called 'alkenes'. e.g.,  $C_2H_4$  is named as '*ethene*' after the name of its corresponding alkane ethane ( $C_2H_6$ ).

The longest carbon chain containing the double bond is chosen as the main chain and the positions of double bond and side chains are indicated by numbering the carbon atoms of this main chain. The lowest possible number is given to the double bond and the side chains are also indicated accordingly.

The names of the first few members of the homologous series of alkenes according to both the systems are given below :

Formula	Corresponding paraffin	Trivial name	IUPAC name
$CH_2 = CH_2$	Ethane ( $C_2H_6$ )	Ethylene	Ethene
$CH_3CH = CH_2$	Propane ( $C_3H_8$ )	Propylene	Propene
$CH_3CH_2CH = CH_2$	Butane ( $C_4H_{10}$ )	$\alpha$ or 1-Butylene	Butene-1
$CH_3CH = CH.CH_3$	Butane ( $C_4H_{10}$ )	$\beta$ or 2-Butylene	Butene-2

## • 4.3. ALKYNES

The first member of alkynes is acetylene hence the name of the series is given as acetylene series. The general molecular formula of this homologous series is  $C_nH_{2n-2}$ . The members of this homologous series has two hydrogen atoms less than the corresponding member of olefin series. All members of this series have at least one triple bond. Alkadienes or dienes are isomeric with alkynes.

### [I] Nomenclature

There are two main systems of nomenclature.

(i) **Trivial system** : Higher members of this series in this system, are named as the alkyl derivatives of acetylene.

(ii) **IUPAC system** : The members of this series are named after the corresponding alkane by changing the suffix 'ane' into 'yne', hence in general they are called 'alkynes'. The rules of numbering of carbon atoms are the same as for alkenes.

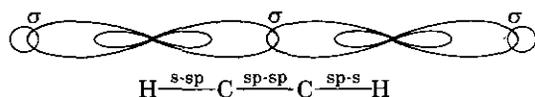
The trivial and IUPAC names alongwith the formulae of few members are given below :

Formula	Corresponding paraffin	Trivial name	IUPAC name
$CH \equiv CH$	Ethane ( $C_2H_6$ )	Acetylene	Ethyne
$CH_3 - C \equiv CH$	Propane ( $C_3H_8$ )	Methylacetylene	Propyne

$\text{CH}_3\text{C}\equiv\text{CCH}_3$	Butane ( $\text{C}_4\text{H}_{10}$ )	Dimethylacetylene	Butyne-2
$\text{CH}_3\text{CH}_2\text{C}\equiv\text{CH}$	Butane ( $\text{C}_4\text{H}_{10}$ )	Ethylacetylene	Butyne-1
$\text{CH}_3\text{CH}_2\text{CH}_2\text{C}\equiv\text{CH}$	Pentane ( $\text{C}_5\text{H}_{12}$ )	<i>n</i> -Propylacetylene	Pentyne-1
$\begin{array}{c} \text{CH}_3\text{CH}-\text{C}\equiv\text{CH} \\   \\ \text{CH}_3 \end{array}$	Pentane ( $\text{C}_5\text{H}_{12}$ )	Isopropylacetylene	3-Methyl butyne-1
$\text{CH}_3\text{CH}_2\text{C}\equiv\text{C}\cdot\text{CH}_3$	Pentane ( $\text{C}_5\text{H}_{12}$ )	Ethylmethylacetylene	Pentyne-2

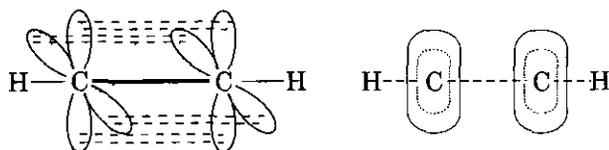
### [II] Orbital Structures of Acetylene

***sp*-hybridisation** : The mixing of an *s* and *p*-orbitals only leads to two co-linear hybrid orbitals known as *sp* hybrid orbitals. This process is called ***sp*-hybridisation**. This gives an angle of  $180^\circ$ . The remaining two *2p* (say  $2p_y, 2p_z$ ) orbitals are left undisturbed and lie perpendicular to each other, e.g., acetylene ( $\text{C}_2\text{H}_2$ ).



Orbital picture of acetylene depicting  $\sigma$ -bonds only

One *sp* hybrid orbital of carbon atom overlaps co-axially with that of another carbon atom to form a sigma ( $\text{C}-\text{C}$ ) bond. The remaining 1 *sp* hybrid orbital of each of the two carbon atoms overlap with one *s*-orbital of two different hydrogen atoms to form two sigma ( $\text{C}-\text{H}$ ) bonds. The  $2p_y$  and  $2p_z$  orbitals perpendicular to each other are thus left on each of the carbon atom. Thus, these form two  $\pi$ -bonds by sideways overlapping and the four lobes of the two  $\pi$ -bonds merge to form a single electron cloud which is symmetrical (cylindrically) about the inter-nuclear axis. The  $\pi$ -bonds formed by relatively poorer sideways overlapping of *2p*-orbitals would be weaker than the  $\sigma$ -bond formed by the efficient overlapping of *sp-sp* orbitals.

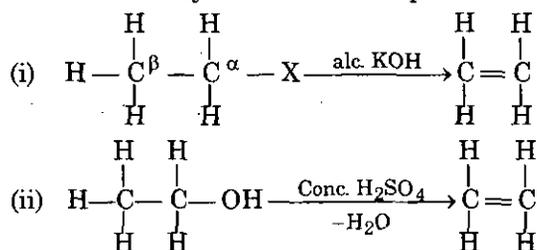


Orbital picture of acetylene depicting the formation of  $\pi$ -bonds

The structure of  $\text{C}\equiv\text{C}$  triple bond in higher alkynes is similar to that mentioned in the case of acetylene.

### [III] Elimination Reactions

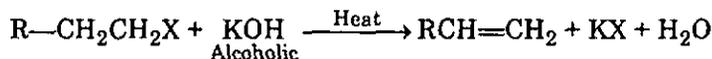
**Elimination reactions** are those in which two atoms or groups attached to two adjacent carbon atoms in a molecule are removed with simultaneous formation of a multiple bond between the two carbon atoms. One of the groups of atoms commonly eliminated as a proton and the other as an atom e.g.



Let us now discuss the mechanism of the above two examples.

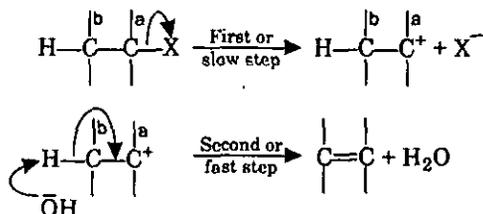
### (1) Dehydrohalogenation of alkyl halides

As we know, an alkyl halide undergoes dehydrohalogenation to form olefin when it is heated with alcoholic KOH.

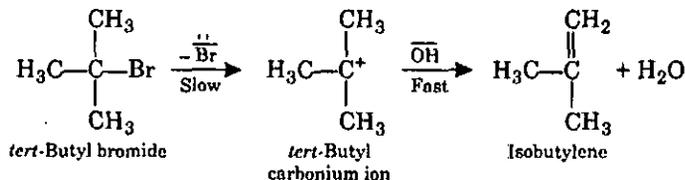


The reaction may proceed through two different mechanisms.

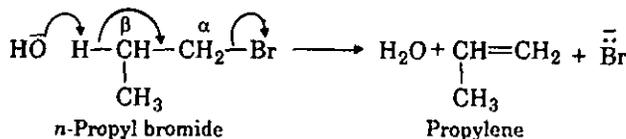
(a) **Two steps elimination reaction mechanism (E<sup>1</sup>):** The first or slow step involves the heterolytic fission of carbon-halogen bond to form a carbonium ion and halide ion. The second or fast step involves the elimination of a proton from β-carbon atom with the help of OH<sup>-</sup>, to produce an olefin.



Since only one molecule, i.e., alkyl halide takes part in the slow or rate determining step, it is called *E<sup>1</sup> mechanism*. The mechanism is found in the case of tertiary alkyl halides as stable tertiary carbonium ions are formed e.g.,

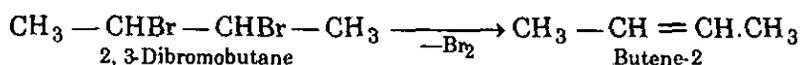


(b) **One step elimination reaction mechanism (E<sup>2</sup>):** This type of mechanism involves the abstraction of a proton from β-carbon atom by a base with the simultaneous loss of a halide ion from the α-carbon of the alkyl halide molecule, e.g.,



The mechanism thus takes place in one step but kinetically it is second order, i.e., first order in substrate (halide) and first order in base.

Dehalogenation reaction also proceeds via *E<sup>2</sup>* mechanism. It is also an example of anti-elimination, i.e., the two halogen atoms depart in opposite directions, e.g., *meso*-2, 3-dibromobutane on debromination produces *trans*-olefin, while the *racemic* form (±) forms *cis*-olefin.

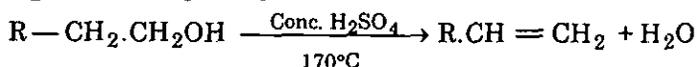


Meso form → *trans*-isomer

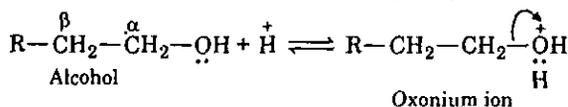
Racemic form → *cis*-isomer

### (2) Dehydration of Alcohols

Alcohols in presence of dehydrating agent such as conc. H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub>, anhydrous ZnCl<sub>2</sub> etc., undergo dehydration to form olefins.



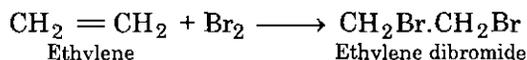
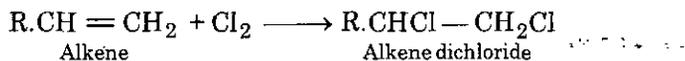
The mechanism of the reaction involves following steps:







(b) **Addition of halogens** : Generally, the reaction is carried out by taking the solutions of reactants in inert solvents like  $\text{CCl}_4$ ,  $\text{CS}_2$  etc. Two halogen atoms add to each double bond forming a dihalide.

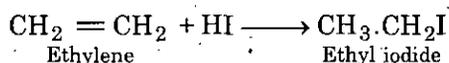


Decolorisation of 5% solution of bromine in carbon tetrachloride is used as a test for alkenes or the double bond.

The order of reactivity amongst the halogens is,

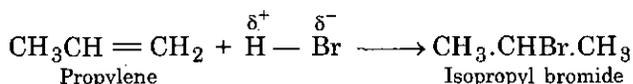


(c) **Addition of halogen acids** : Alkenes add halogen acids to form alkyl halides. The order of reactivity is  $\text{HI} > \text{HBr} > \text{HCl}$ .

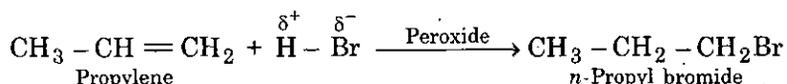


### Markownikoff's Rule

Markownikoff's rule is used to predict the reaction product of the addition of a polar molecule to an unsymmetrical olefin. It states that : *The negative part of the addendum (molecule which adds) attaches to that olefinic carbon of unsymmetrical olefin which contains the lesser number of hydrogen atoms, i.e., more substituted carbon e.g., addition of HBr to propylene gives isopropyl bromide.*



However, when the addition of HBr is carried out in presence of a peroxide (benzoyl peroxide etc.), the addition is abnormal, i.e., anti to Markownikoff's rule. This is commonly referred to as **peroxide effect** or **Kharasch's effect** or **anti-Markownikoff's addition**.

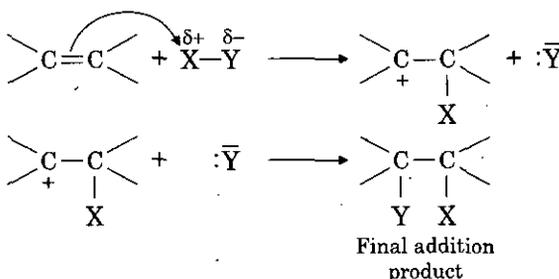


### Mechanism of Electrophilic Addition Reactions

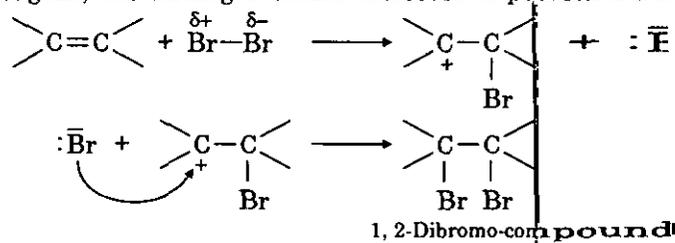
Addition reactions in alkenes generally proceed through ionic mechanism. In few cases, however, they may proceed through free radical mechanism.

#### [I] Ionic Mechanism

This is a two step mechanism. In the first step, the addition molecule ( $\text{X}-\text{Y}$ ), on coming close to the  $\pi$ -electron, undergoes polarisation ( $\text{X}^{\delta^+}-\text{Y}^{\delta^-}$ ). At the same time, the  $\pi$ -electron pair undergoes electromeric displacement and migrates to one of the  $\pi$ -bonded carbon atoms, from where it attacks the electrophilic end ( $\text{X}^{\delta^+}$ ) of the adding molecule. This attack brings about the union of the electrophilic end to the adding molecule with the olefinic carbon atom to which the  $\pi$ -electron pair had migrated, forming a carbonium ion (the product of electrophilic addition). Simultaneously, the nucleophilic portion ( $:\text{Y}^-$ ) of the adding molecule is released. In the second step, the nucleophile ( $:\text{Y}^-$ ) is bonded to the positively charged carbon atom of the carbonium ion to produce the final compound.



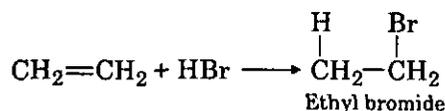
(i) **Addition of symmetrical reagents, like halogens :** In the addition of bromine, which is a symmetrical reagent, the adding bromine molecule is polarised ( $\text{Br}^{\delta+} - \text{Br}^{\delta-}$ ) on its approach to the  $\pi$ -electron pair of the olefin. The  $\pi$ -electron pair then attacks the positive end of bromine molecule, uniting one of the olefinic carbon atom with this end and simultaneously releasing  $:\text{Br}^-$ .



The order olefinic carbon atom, thus acquires a positive charge to form a carbonium ion. In the second step, the  $:\text{Br}^-$  an ion released in the first step, combines with the carbonium ion forming the final addition product.

The symmetrical or unsymmetrical nature of the olefin in such cases does not change the nature of the product.

(ii) **Addition of unsymmetrical reagents in symmetrical olefins :** The addition of HBr to ethylene is an example of electrophilic addition.

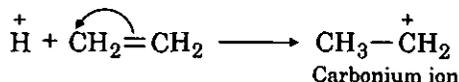


The mechanism of the reaction involves the following steps :

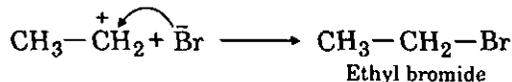
**Step 1 :** Hydrogen bromide gives a proton ( $\text{H}^+$ ) and bromide ion ( $\text{Br}^-$ ).



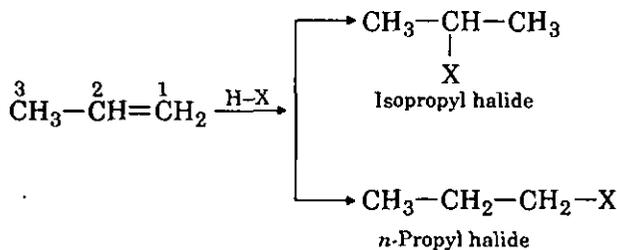
**Step 2 :** The electrophile attacks the  $\pi$ -bond of ethylene to give a carbonium ion.



**Step 3 :** The nucleophile attacks the carbonium ion to give the addition product.



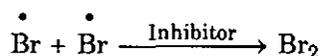
(iii) **Addition of unsymmetrical reagents, like H-X in unsymmetrical olefins :** In such reactions, the positive part of the reagent becomes attached to the double-bonded carbon atom which bears the greatest number of hydrogen atoms. Theoretically, two products are formed, e.g.,



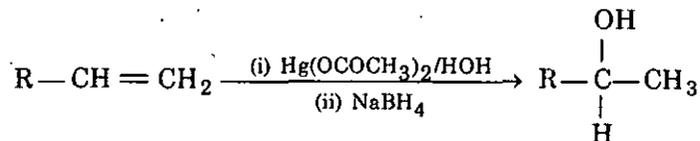
In actual reaction, however, isopropyl halide is the main product. This preferential formation of isopropyl halide may be due to the +E effect of methyl group in propene. When the nucleophile unites with carbon atoms (may be on  $\text{C}_1$  or  $\text{C}_2$ ), carbonium ions formed are the isopropyl (secondary) carbonium ion ( $\text{CH}_3-\overset{+}{\text{C}}\text{H}-\text{CH}_3$ ) and n-propyl carbonium ion ( $\text{CH}_3-\text{CH}_2-\overset{+}{\text{C}}\text{H}_2$ ) due to hyperconjugation.



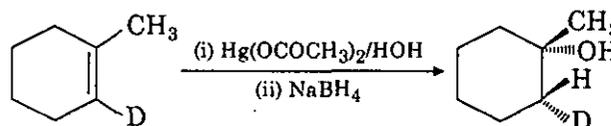
(iii) Termination :



**Oxymercuration-demercuration :** Addition of alkene with mercuric acetate in presence of water is known as *oxymercuration*. In this case, product is formed by the formation of bridged carbocation which acts as reaction intermediate. The addition of sodium borohydride gives alcohol. This step is called *demercuration*. The overall reduction is also known as *oxymercuration reduction*.

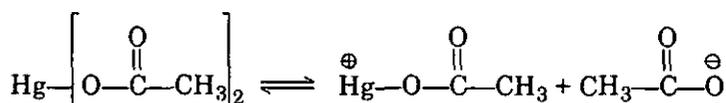


Experimentally, it has been seen that the product of the reaction is a result of an *anti* addition reaction. e.g.,

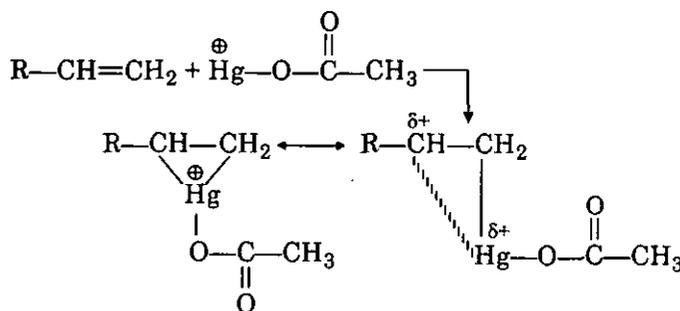


*Anti* addition can only be explained if product formation occurs by the formation of a cyclic intermediate.

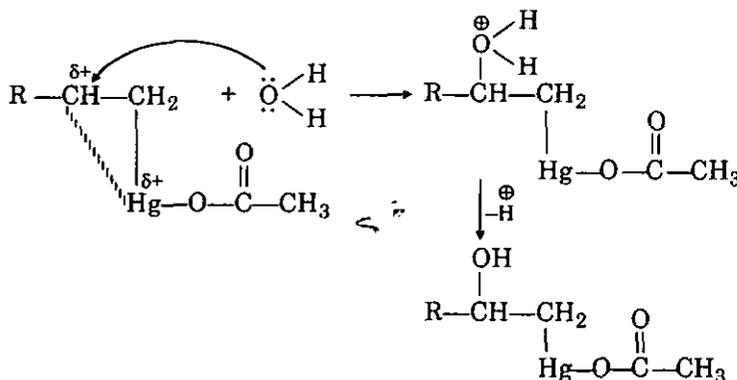
**Mechanism**



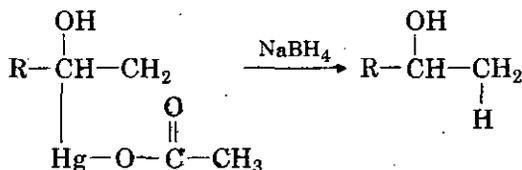
**1st step :**



**2nd step :** In this step, nucleophile attacks on the opposite face of Hg. Nucleophile will attack on the carbon which has more carbocation character.

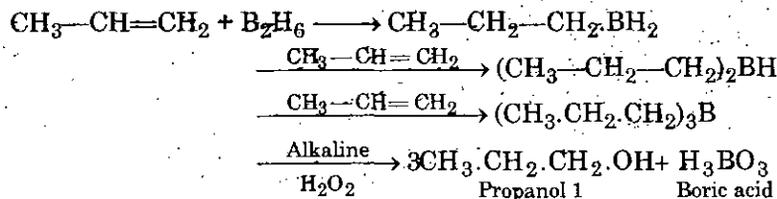


**3rd step :** Sodium borohydride changes C—Hg bond into a C—H bond. Because the reaction occurs due to loss of mercury, it is called demercuration.



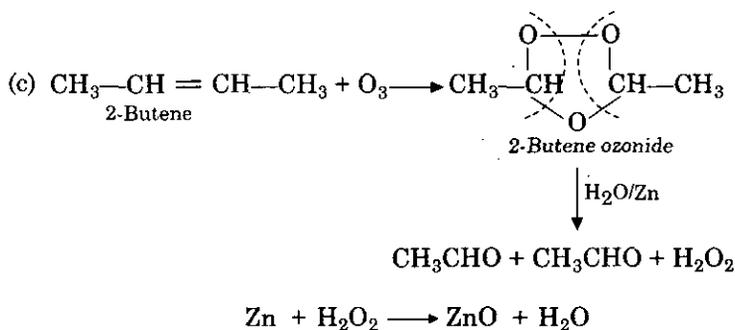
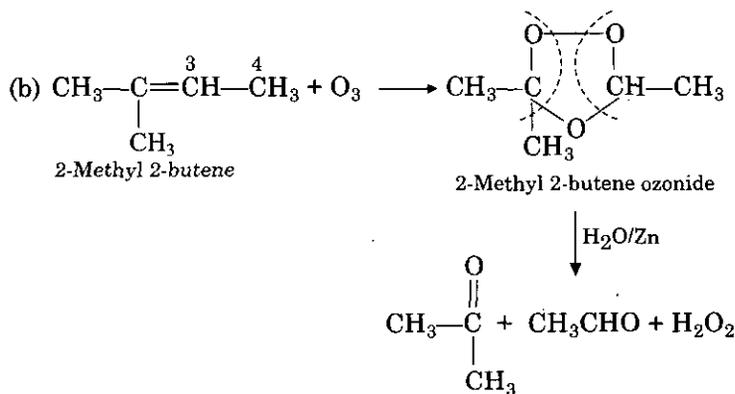
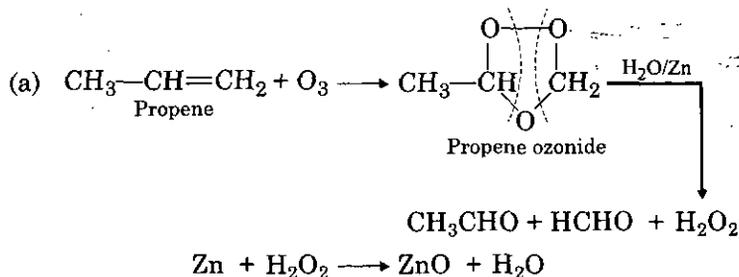
In the product both H and —OH are *anti* to each other.

**Hydroboration oxidation** : Alkenes reacts with diborane to form trialkyl boranes which on oxidation with alkaline  $\text{H}_2\text{O}_2$  give alcohols.



**Ozonolysis** : The addition of ozone to an unsaturated hydrocarbon to form an ozonide followed by its decomposition to get the carbonyl compound is known as ozonolysis. In the case of alkenes the chain breaks up at the original position of the double bond and aldehydes or/and ketones are obtained.

The ozonide can be hydrolysed or reduced. The hydrolysis is done in the presence of reducing agent, zinc dust. Zinc dust prevents the formation of  $\text{H}_2\text{O}_2$  so that the oxidation of carbonyl compounds do not take place. Reduction is done by zinc and acid or hydrogen in the presence of nickel.



From the ozonolysis of various alkenes, it has been concluded that :

(i) An alkene of the type  $R-CH=CH-R$  gives only one aldehyde.

(ii) An alkene of the type  $R-CH=CH-R'$  gives a mixture of two different aldehydes.

(iii) An alkene of the type  $R-\underset{\substack{| \\ R}}{C}=CH-R'$  gives a mixture of a ketone and an aldehyde.

(iv) An alkene of the type  $R-\underset{\substack{| \\ R}}{C}=\underset{\substack{| \\ R}}{C}-R$  gives only one ketone.

(v) An alkene of the type  $R-\underset{\substack{| \\ R}}{C}=\underset{\substack{| \\ R'}}{C}-R'$  gives a mixture of two different ketones.

(vi) A diene of the type  $R-CH=CH-CH=\underset{\substack{| \\ R}}{C}-R$  gives

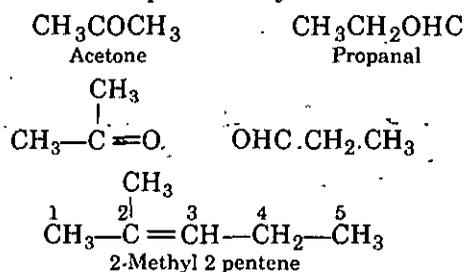
three products *i.e.*, an aldehyde, ketone and dialdehyde.

(vii) A diene of the type  $R-CH=CH-CH=CH-R$  gives only two products — an aldehyde and dialdehyde.

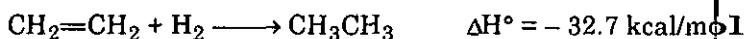
(viii) A diene of the type  $R-\underset{\substack{| \\ R}}{C}=CH-CH=\underset{\substack{| \\ R}}{C}-R$  gives only two products — a ketone and dialdehyde.

### Location of the Position of Double Bond in an Alkene

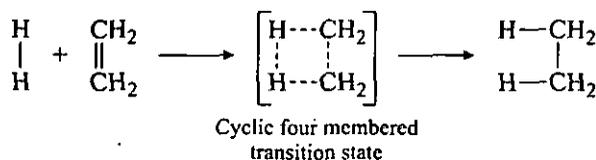
Ozonolysis is the best method for locating the position of double bonds in an unknown alkene. The oxygenated carbon atoms in carbonyl compounds obtained by ozonolysis are those which were joined by a double bond in the original alkene. For example, an alkene on ozonolysis gives two carbonyl compounds acetone and propanal. For establishing the structure of an alkene, we write down the structural formulae of carbonyl compounds. Remove oxygen atom on ketonic or aldehydic group and then join the two carbonyl carbon atoms of the products by a double bond.



### Reduction

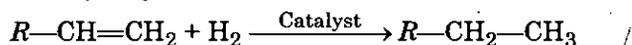


Although addition of hydrogen to  $\pi$  bond is an exothermic reaction, even then the rate of reaction is not appreciable without an appropriate catalyst. This is because of the high energy of activation associated with the addition. In the absence of catalyst formation of product takes place via the formation of cyclic four membered transition state.

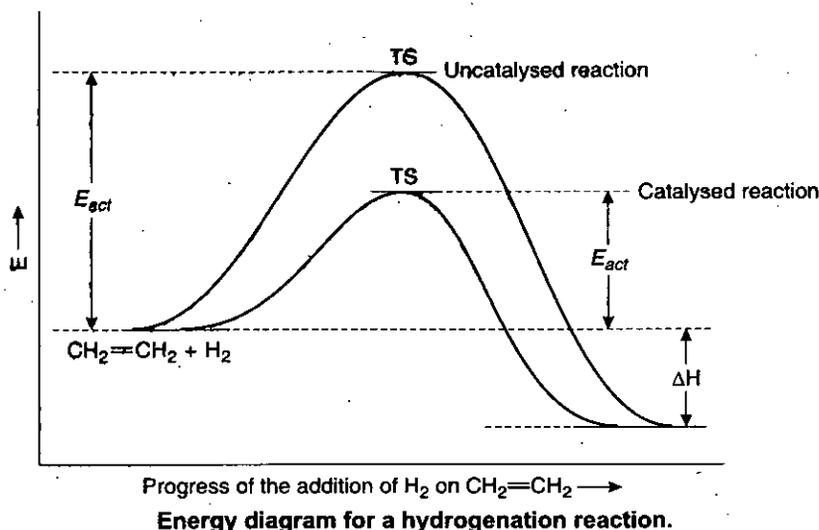


This mechanism is impractical due to high energy. However reaction proceeds smoothly when a catalyst is added.

Catalysis for hydrogenation include finely divided platinum, palladium, ruthenium, rhodium and nickel. The most famous of these include Adam's catalyst and Raney nickel. Adam's catalyst consists of finely divided platinum metal, called platinum black. It is used in low pressure (1 to 2 atm) hydrogenations. Raney nickel is also used for low pressure hydrogenations. It is less active than Pt and Pd.



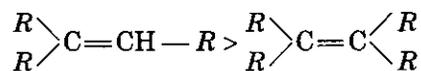
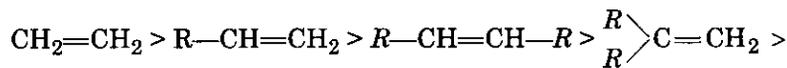
How does a catalyst ease the course of a hydrogenation reactions? Experimental evidence supports the theory that first the hydrogen molecules are absorbed onto the metallic surface of the catalyst, then the  $\sigma$ -bonds of hydrogen molecules are broken, and metal-H bonds are formed. The alkene is also absorbed onto the metallic surface with its  $\pi$  bond interacting with the empty orbitals of the metal. The alkene molecule moves around on the surface until it collides with a metal bonded hydrogen atom, undergoes reaction, and then leaves as the hydrogenated product.



From the given mechanism the following conclusions can be drawn :

(i) Reduction reaction of alkene is always catalytic reduction and this reaction is **syn addition** in which product formation takes place by the formation of transition state (TS). Thus addition of hydrogen is stereospecific reaction.

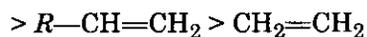
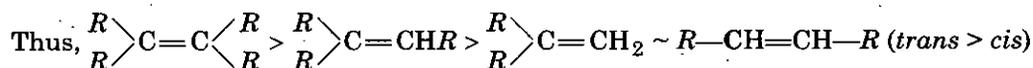
(ii) Addition takes place by the formation of TS therefore least substituted alkene will be most reactive for this reaction.



Reactivity in decreasing order for addition of  $H_2$

(iii) Hydrogenation is always exothermic reaction and

$$\text{Stability of alkene} \propto \frac{1}{\text{Heat of Hydrogenation}}$$



(i) Stability of alkenes in decreasing order

(ii) Heat of hydrogenation in increasing order

(iv) Reactivity of alkene for reduction  $\propto$  Heat of hydrogenation.

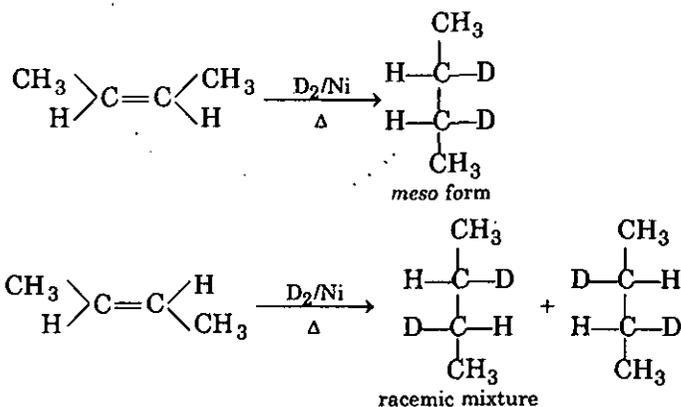
(v) CSM is the word from which stereochemistry of *syn* addition reactions can be concluded as follows :

C (means *cis* alkene) on

S (means *syn* addition) gives

M (*meso* form)

For example :



**Oxidation :** Oxidation of alkenes is of two types :

(1) Oxidation of the  $\pi$  bond without cleavage of the  $\sigma$  bond i.e. **oxidation without cleavage.**

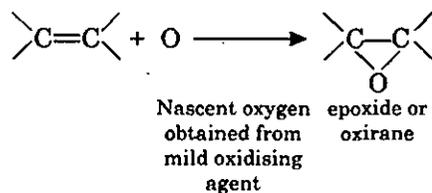
(2) Oxidation of the  $\pi$  bond with cleavage of the  $\sigma$  bond i.e. **oxidative cleavage of alkenes.**

Both these types of oxidation reactions are discussed here.

### Oxidation Without Cleavage

This oxidation is given by mild oxidising agents. The products of the oxidation without cleavage are either epoxides or 1, 2 diols.

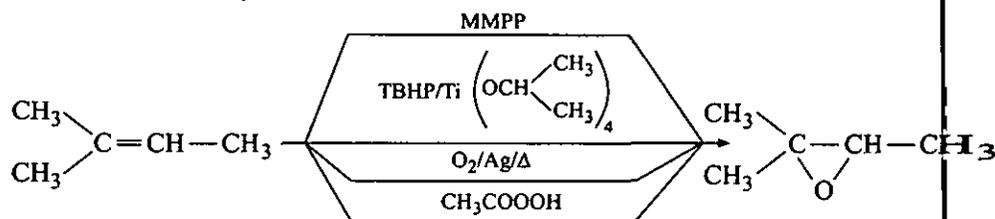
(A) **Formation of epoxides :** Formation of epoxide takes place as follows :

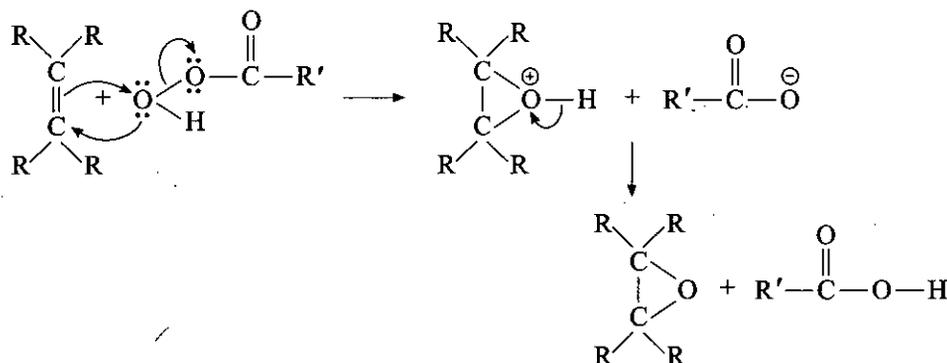


Following four reagents give epoxide formation :

(i)  $\text{O}_2/\text{Ag}/\Delta$ , (ii) Organic peracids :  $\text{RCOOOH}$ , the most common peracid is *meta* bromoperbenzoic acid. 1 : 3  $\text{COOOH} \cdot \text{Br} \cdot \text{C}_6\text{H}_4$ , (iii) *Tertiary* butyl hydroperoxide (TBHP) in the presence of titanium isopropoxide. (iv) Magnesium monoperoxyphthalate (MMPP).

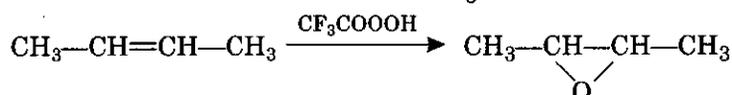
These reactions may be represented as :



**Mechanism :**


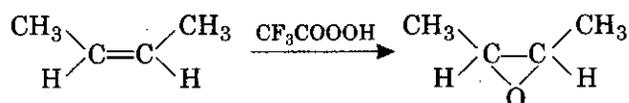
This reaction is known as **Prilezhaev reaction**.

For epoxidation best result is obtained from  $\text{CF}_3\text{COOOH}$ .



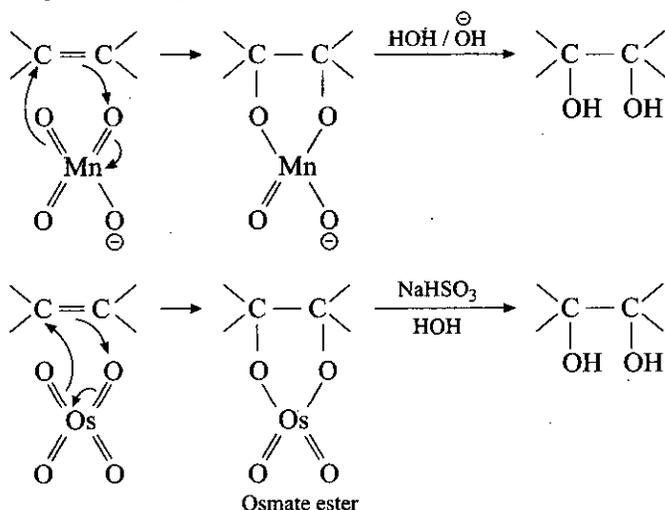
It is important to note that alkene in which double bond is conjugated with strong electron withdrawing group such as  $-\text{COOC}_2\text{H}_5$ ,  $-\text{CHO}$  does not give epoxidation reaction, e.g.  $\text{CH}_2=\text{CH}-\text{COOC}_2\text{H}_5$  and  $\text{C}_6\text{H}_5-\text{CH}=\text{CH}-\text{CHO}$ .

The epoxidation reaction is stereospecific and addition of oxygen atom across double bond is always *syn*.

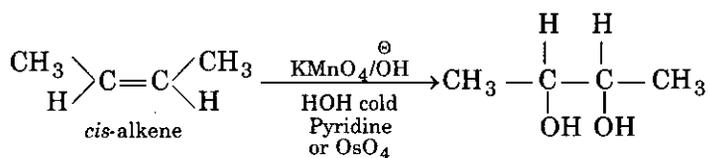


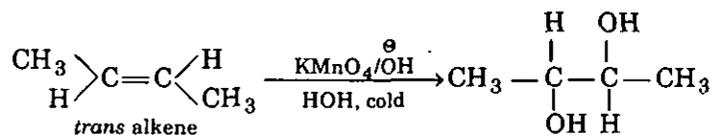
This epoxidation followed by hydrolysis can be used for the preparation of *trans* diols from the alkenes.

**(B) Diol Formation :** For 1, 2-diol formation from alkene a cold alkaline aqueous solution of potassium permanganate (Baeyer's reagent) and Osmium tetroxide ( $\text{OsO}_4$ ) are used. But  $\text{OsO}_4$  is both expensive and toxic.

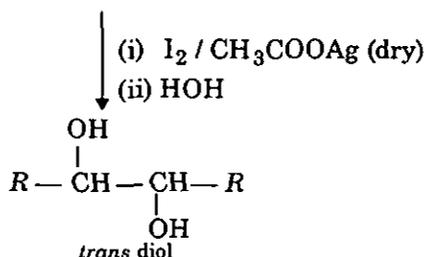
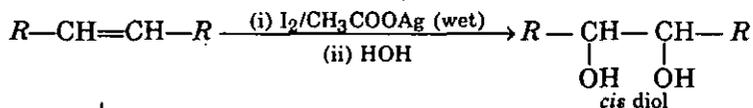


(i) Thus the overall reaction is addition of OH group on both the doubly bonded carbons and addition is *syn*. Thus *cis* alkenes will give *meso* form whereas *trans* will give *dl* mixture.

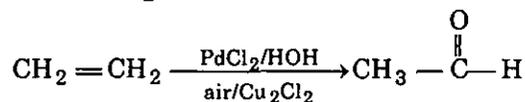




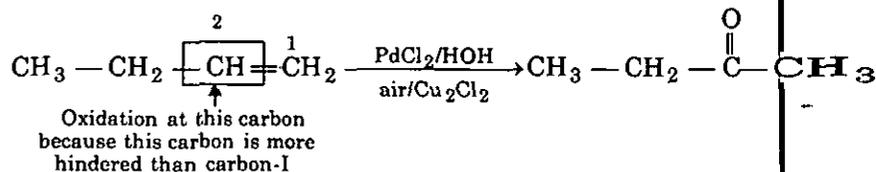
(ii)  $\text{I}_2/\text{CH}_3\text{COOAg}$  also gives 1, 2-diol formation with alkenes. Stereochemistry of the product depends on nature of  $\text{CH}_3\text{COOAg}$ .



(c) **Oxidation of alkenes into carbonyl compounds : Wacker Process**  
Oxidation of ethylene, mono substituted and 1, 2-disubstituted alkenes into carbonyl compound in the presence of  $\text{PdCl}_2$ ,  $\text{HOH}$ , air and  $\text{CuCl}$  is known as Wacker process.



In the case of unsymmetrical alkenes more hindered olefinic carbon converts into carbonyl group.



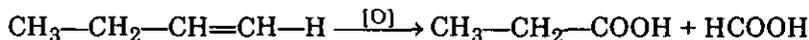
### Oxidation with cleavage : Oxidative cleavage

(A) **Cleavage with hot basic  $\text{KMnO}_4$**  : The product of oxidation reaction depends upon the structure of the alkene.

(1) Mono substituted vinylic carbon converts into carboxylic group by  $\text{KMnO}_4/\text{OH}^\ominus$

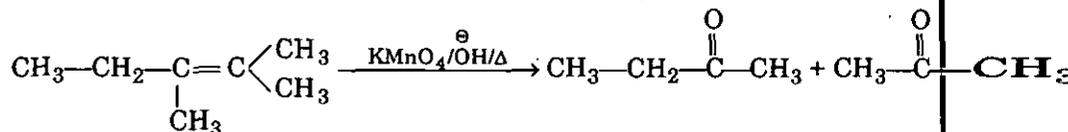


**Note** : Terminal alkene gives formic acid as one of the products which further undergoes oxidation into  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . This reaction takes place only under drastic conditions.

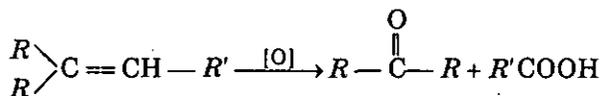


Thus loss of one carbon in this reaction indicates that alkene is a terminal alkene.

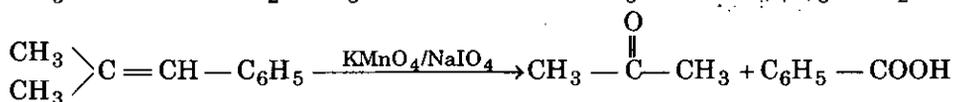
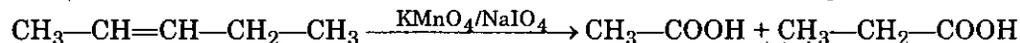
(2) Disubstituted vinylic carbon converts into keto group by the reagent.



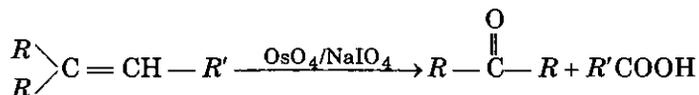
**Note** : If one vinylic carbon is monosubstituted and other is disubstituted the product will be mixture of ketone and monobasic acid.



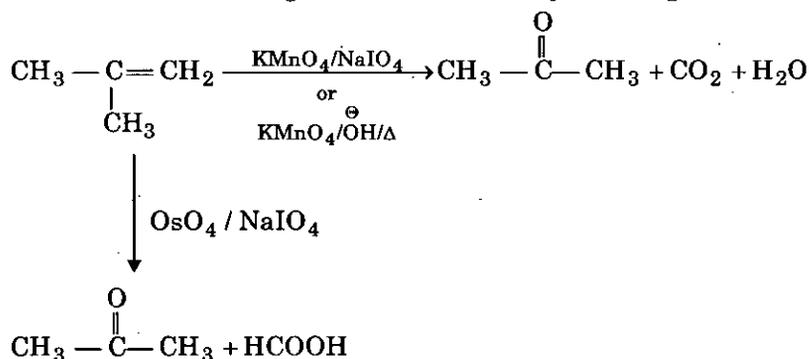
**(B) Cleavage with  $\text{NaIO}_4/\text{KMnO}_4$  (known as Lemieux reagent) :** The results obtained by this reagent is identical to the results obtained by  $\text{KMnO}_4/\text{OH}^-/\Delta$



**(C) Cleavage with  $\text{OsO}_4/\text{NaIO}_4$  (This is also known as Lemieux reagent) :** In this case also monosubstituted vinylic carbon converts into carboxylic group and disubstituted vinylic carbon into keto group.



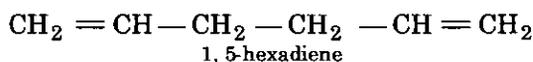
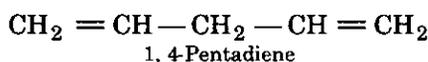
**Note :**  $\text{HCOOH}$  does not undergo further oxidation by this reagent.



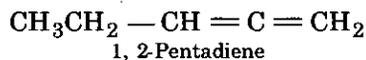
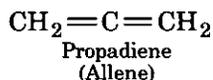
## Dienes

Dienes are the alkenes containing two  $\text{C} = \text{C}$  double bonds. These have the general formula  $\text{C}_n\text{H}_{2n-2}$  and are isomeric with alkynes. These can be of three types :

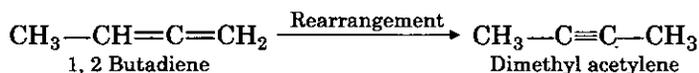
**(1) Isolated dienes :** They contain two double bonds separated by two or more saturated carbon atoms, *e.g.*,



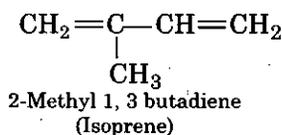
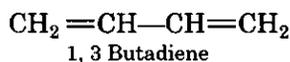
**(2) Cumulative dienes (Cumulenes or allenes) :** They contain two double bonds at adjacent positions, *e.g.*,



They are less stable and possess tendency to rearrange into hydrocarbons containing triple bond, *e.g.*,

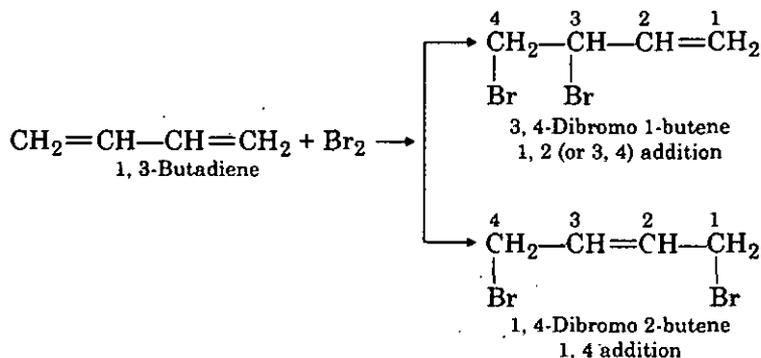


**(3) Conjugated dienes :** They contain alternating system of single and double bonds, *e.g.*,



### 1, 2- and 1, 4-Addition Reactions in Conjugated Dienes

**Addition of halogens :** It reacts with  $\text{Cl}_2$  or  $\text{Br}_2$  in the presence of  $\text{CCl}_4$  to give a mixture of two dichloro or dibromo compounds.

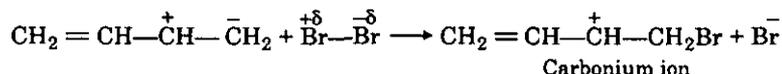


#### Mechanism of 1, 4 and 1, 2 (or 3, 4) addition

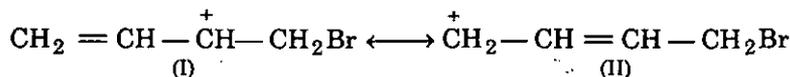
(i) At the approach of reagent (bromine), butadiene undergoes electromeric effect



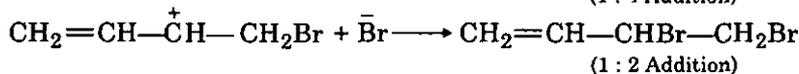
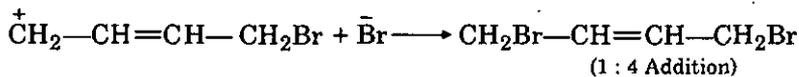
(ii) In ionising solvent, bromine molecule is partially polarised as  $\text{Br}^{\delta+}-\text{Br}^{\delta-}$ . Polarised bromine molecule combines with partially polarised butadiene producing carbonium ion and negative bromide ion.



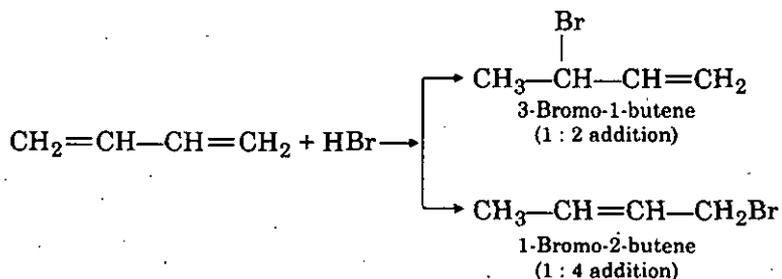
The carbonium ion is a resonance hybrid of the following structures :



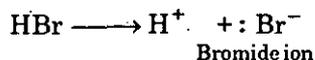
The negative bromide ion then combines with the positive carbon atom producing a mixture of 1 : 4 and 1 : 2 (or 3 : 4) addition products.



**Addition of halogen acids :** At low temperatures, 1 : 2 addition predominates whereas at high temperatures, 1 : 4 addition predominates.



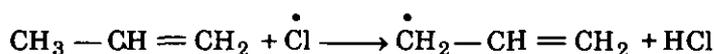
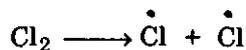
#### Mechanism



Proton attacks a double bond according to Markownikoff's rule to give resonance stabilised carbonium ion.



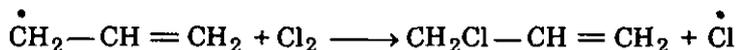
The substitution reaction occurs by a free radical mechanism. After initiation abstraction of a hydrogen from the methyl group of alkene forms a stable allylic radical



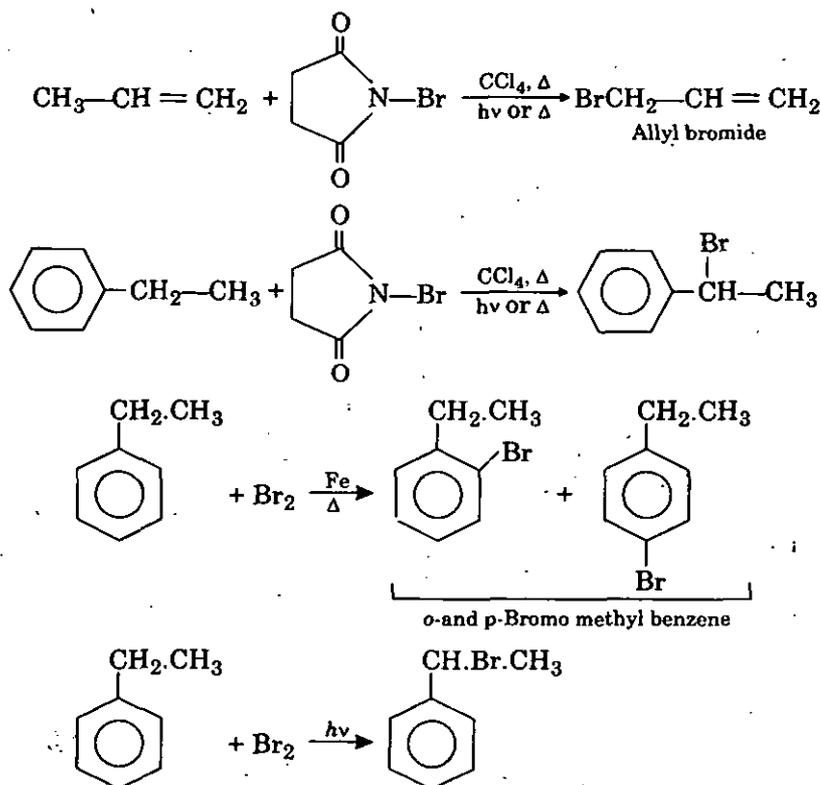
The allylic radical is stabilised by resonance.



The allylic radical survives for a long period and is thus able to collide with chlorine molecule to abstract Cl from Cl<sub>2</sub> and form the allyl chloride.

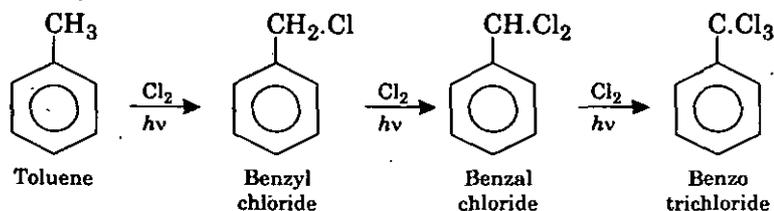


At higher temperatures, the normal addition of chlorine atom to the double bond becomes unfavourable. At room temperature, allylic substitution is brought about by N-bromo succinimide (NBS) in presence of non-polar solvents. The reagent introduces bromine at the allylic and benzylic positions and not at other positions. The reaction is catalysed by light or by some source of free radicals.



In allylic halogenation reaction, the reactivity of allylic carbons is in the order  $\text{tert-allylic carbon} > \text{sec-allylic carbon} > \text{primary allylic carbon}$ .

**Side chain Halogenation :** When Cl<sub>2</sub> gas is passed through boiling toluene in the presence of UV light side chain substitution takes place as follows :



**Mechanism :** The mechanism of the above reactions may be given as :

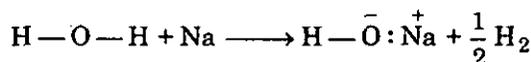


### [VI] Reactions of Alkynes

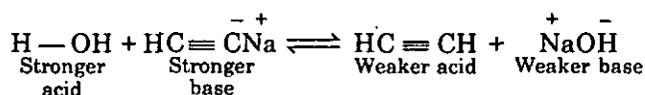
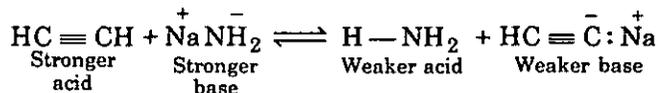
1. **Acidity** : Acetylene reacts with sodium to form sodium acetylide and hydrogen gas.



This is similar to the reaction of sodium with water.



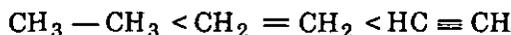
This suggests that hydrogen in acetylene is acidic in nature. It is known that weaker acid is displaced from its salt by a stronger acid. While  $\text{C}_2\text{H}_2$  displaces  $\text{NH}_3$  from its salt sodamide ( $\text{NaNH}_2$ ), water displaces acetylene from its salt sodium acetylide.



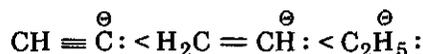
So, acetylene is a stronger acid than ammonia but weaker acid than water, i.e.,



**Relative acidities of ethane, ethylene and acetylene** : The increasing order of acidities of these hydrocarbons is :



Conversely, the increasing order of basicities of anions resulting from these hydrocarbons is :



In order to account for the above facts, two explanations have been given :

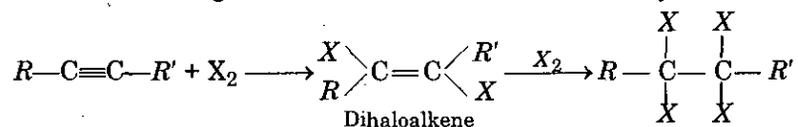
(1) In  $\text{CH} \equiv \overset{\ominus}{\text{C}} :$ ,  $\text{CH}_2 = \overset{\ominus}{\text{C}} \text{H}$  and  $\text{C}_2\text{H}_5 : \overset{\ominus}{\text{C}}$ , the unshared pair of electrons occupies an  $sp$ ,  $sp^2$  and  $sp^3$  orbital, respectively. As we move along  $sp$ ,  $sp^2$  and  $sp^3$  series, the  $s$ -character of the hybrid orbital increases and the  $p$ -character decreases. An electron in an  $s$ -orbital is closer to the nucleus and is held more tightly. But an electron in a  $p$ -orbital is farther from the nucleus and is held less tightly. So, the electron pair in  $\text{C}_2\text{H}_5 : \overset{\ominus}{\text{C}}$  should be held most loosely and in  $\text{CH} \equiv \overset{\ominus}{\text{C}}$  should be most tightly. Therefore, the electron pair in  $\text{C}_2\text{H}_5 : \overset{\ominus}{\text{C}}$  should be most available, while in  $\text{CH} \equiv \overset{\ominus}{\text{C}}$  should be least available, for protonation. Thus, in the above series, the carbanion  $\text{C}_2\text{H}_5 : \overset{\ominus}{\text{C}}$  should be the strongest base and  $\text{CH} \equiv \overset{\ominus}{\text{C}}$  should be the weakest base. Conversely, acetylene should be most acidic, while ethane should be least acidic.

(2) According to this explanation, the C—H bonds in ethane, ethylene and acetylene are  $sp^3-s$ ,  $sp^2-s$  and  $sp-s$  bonds, respectively. Now  $sp^3$  orbital has the minimum  $s$ -character and  $sp$ -orbital has the maximum  $s$ -character in  $sp$ ,  $sp^2$  and  $sp^3$  orbitals. It is known that greater the  $s$ -character of an orbital, the more closely are the electrons held to the nucleus in that orbital. It is thus expected that  $sp$  electrons in acetylene are held more closely to the nucleus than  $sp^2$  electrons in ethylene or  $sp^3$  electrons in ethane. Thus,  $sp$  hybridised carbon would attract the electron pair forming the C—H bond of acetylene. Similarly, the  $sp^3$  hybridised carbon in ethane compared with  $sp^2$  hybridised carbon in ethylene would have less attraction for electron pair.

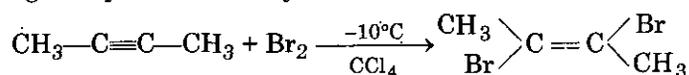
forming the C—H bond in them. It means that C—H bond in ethylene will be less ionic than in acetylene and the C—H bond in ethane will be less ionic than in ethylene. This means that the hydrogen attached to a doubly bonded carbon in ethylene would have less tendency to depart as proton ( $H^+$ ) than the hydrogen attached to a triply bonded carbon in acetylene. Similarly, the hydrogen attached to a single bonded carbon in ethane would have less tendency to depart as proton than the hydrogen attached to a doubly bonded carbon in ethylene. On this basis, we can infer that ethane would be less acidic than ethylene and ethylene will be less acidic than acetylene.

## 2. Electrophilic Addition Reactions

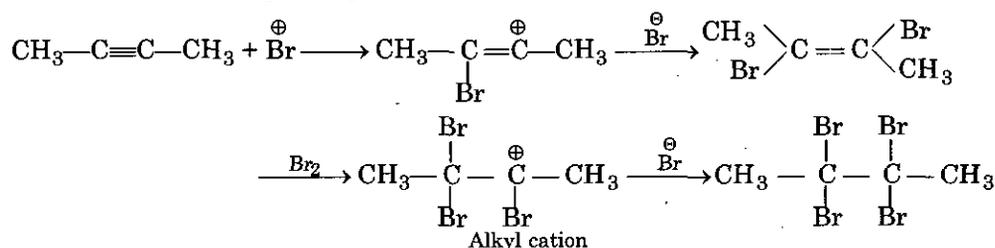
(i) **Addition of Halogens** : Alkynes undergo the same kind of addition reactions with  $Cl_2$  and  $Br_2$  as that alkenes undergo. The major difference is that an alkyne reacts with two molecules of halogens while an alkene reacts with only one molecule.



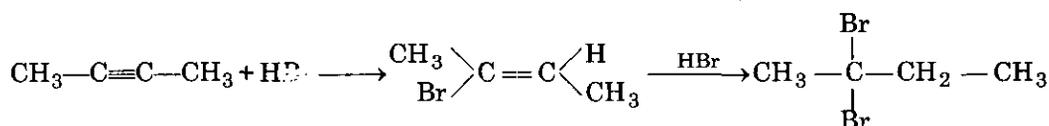
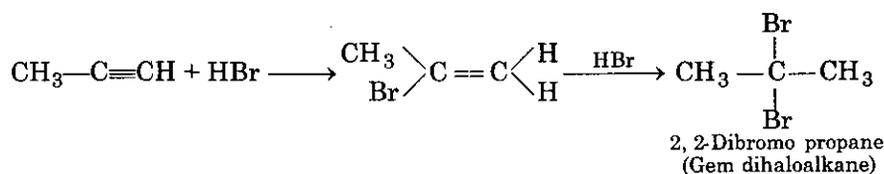
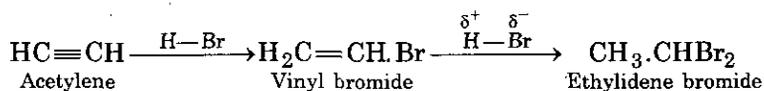
Evidently dihalo alkene is an intermediate product which is formed at low temperature and by the addition of calculated amount of halogen. This addition of halogen is predominantly an **anti** addition



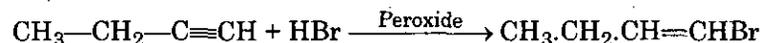
The **mechanism** may be represented as :



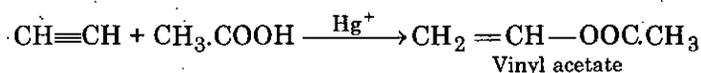
(ii) **Addition of halogen acids** : First, molecule of halogen acid adds to form vinyl halide. The addition of second molecule of halogen acid follows Markownikov's rule to form ethylidene halides.

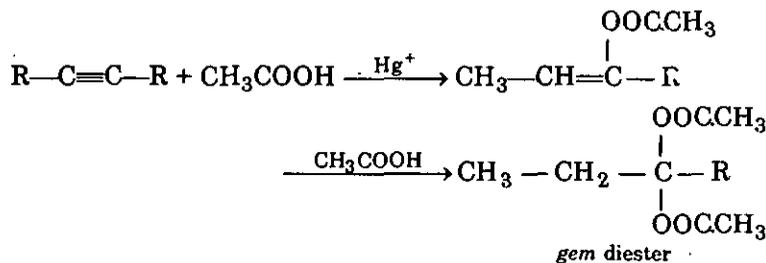


HBr is added according to *anti* Markovnikov manner in presence of peroxide.

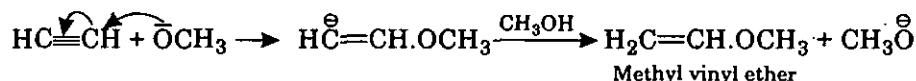


(iii) **Addition of Acetic Acid** : In the presence of mercurous ion, acetic acid adds to alkynes forming either an enol ester or *gem* diester

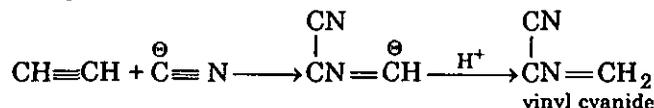




**3. Nucleophilic Addition Reaction :** The addition reaction discussed earlier proceed via electrophilic addition mechanism (i.e., an electrophile adds first). However, alkynes also add alcohols to form unsaturated ethers, the mechanism of the addition is believed to be nucleophilic, i.e., a nucleophile adds first, e.g., when acetylene is passed into methanol at 200°C in presence of potassium methoxide and under high pressure, methyl vinyl ether is obtained. The mechanism of the reaction is :

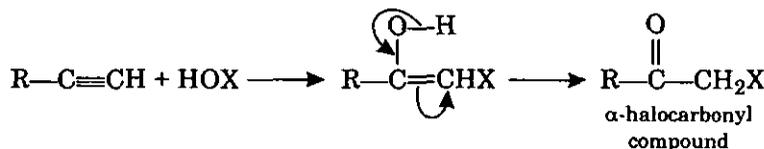


Cyanide ion (CN<sup>-</sup>) reacts with acetylene to yield vinyl cyanide. Cyanide ion is a stable nucleophile to produce a less stable and more basic vinyl anions which combine with H<sup>+</sup> to yield vinyl cyanide

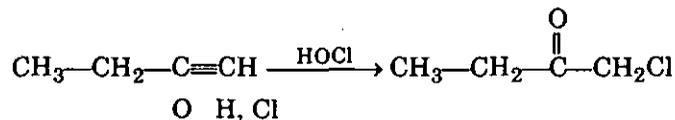


**4. Hydration of alkynes :** In this reaction carbonyl compounds are formed.

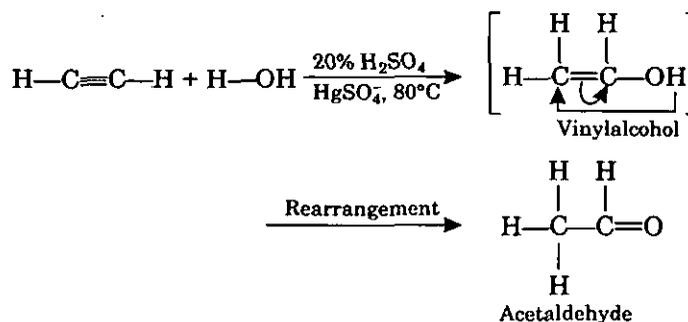
(i) **Addition of HOX :** Alkyne reacts with HOX to give haloenol, which undergoes tautomerisation to give α-halocarbonyl compound.



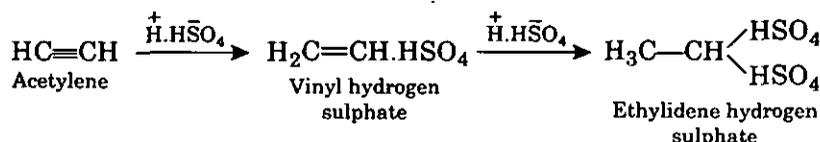
This reaction may also be given as :

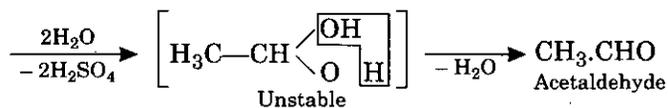


(ii) **Addition of water :** When an alkyne is passed through a dilute (20%) solution of H<sub>2</sub>SO<sub>4</sub> at 80°C in presence of HgSO<sub>4</sub> as catalyst, addition of one molecule of water takes place resulting into the formation of a carbonyl compound.

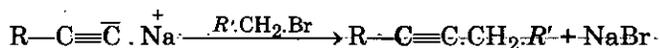
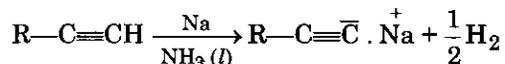
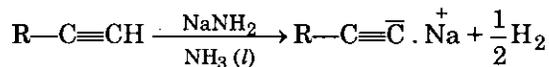


Actually, the reaction proceeds in the following manner.

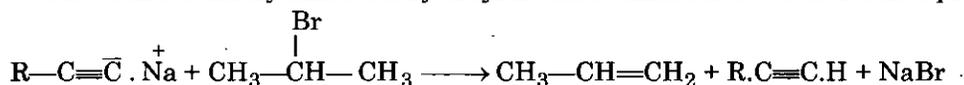




**5. Alkylation of Alkynes :** Since terminal |H| is a very weak acid hence it forms salt with strong base such as  $\text{NaNH}_2$  and molten metal. Sodium salt behaves as nucleophile as well as strong base, which reacts with primary alkyl halides to give alkyl derivative of alkynes. It may be presented as :

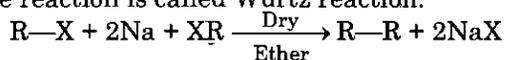


But with secondary and tertiary alkyl halides elimination reaction takes place.

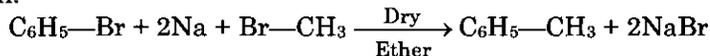


## • SUMMARY

- The general formula of alkanes, alkenes and alkynes in  $\text{C}_n\text{H}_{2n+2}$ ,  $\text{C}_n\text{H}_{2n}$  and  $\text{C}_n\text{H}_{2n-2}$  respectively.
- Only carbon and hydrogen containing compounds are called hydrocarbons.
- **Wurtz reaction :** When sodium reacts with alkyl halide in the presence of dry ether, the reaction is called Wurtz reaction.



- **Wurtz-Fittig's reaction :** When sodium reacts with alkyl halide and aryl halide in the presence of dry ether, the reaction is called Wurtz-Fittig's reaction.



- **Elimination reaction :** The reaction in which two atoms or groups attached to two adjacent carbon atoms in a molecule are removed with simultaneous formation of a multiple bond between the two carbon atoms is called elimination reaction.
- **Saytzeff's rule :** When two olefins are formed by dehydrohalogenation, the one which is more substituted predominates.
- Alkynes may be prepared by dehydrohalogenation of alkene dihalides.
- The greater the reactivity of a species, less will be selectivity.
- The relative rates of formation of alkyl radical by a chlorine free radical is :  
Tertiary > Secondary > Primary
- **Markownikov's rule :** When an unsymmetrical reagent adds to an unsymmetrical double bond, the positive part of the reagent becomes attached to the double-bonded carbon atom which bears the greatest number of hydrogen atom.
- **Ozonolysis :** The addition of ozone to an unsaturated hydrocarbon to form an ozonide followed by its decomposition to get carbonyl compounds is known as ozonolysis.
- Oxidation of alkenes is of two types : (i) Oxidation of the  $\pi$ -bond without cleavage of the  $\sigma$ -bond and (ii) Oxidation of the  $\pi$ -bond with cleavage of the  $\sigma$ -bond.
- In conjugated dienes two types of addition reactions takes place i.e. 1 : 2 and 1 : 4 addition reaction.
- Acetylene is a weak acid.
- Alkynes react with hypochlorous acid and water in the presence of dil.  $\text{H}_2\text{SO}_4$  and  $\text{HgSO}_4$  to yield carbonyl compounds.

• STUDENT ACTIVITY

1. Write a note on Wurtz or Wurtz-Fittig's reaction.

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2. Discuss the preparation of alkenes by Hofmann's elimination reaction.

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3. State and explain halogenation of alkanes.

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4. State and explain Markownikov's and anti Markownikov's reactions.

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5. Write a short note on ionic mechanism of Markownikov's reaction.

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6. Discuss the ozonolysis of 1-butene.

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7. Describe the oxidation reactions with and without  $\sigma$ -bond cleavage.

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8. Discuss 1 : 2 and 1 : 4 addition reaction of 1, 3-butadiene.

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9. Discuss the catalytic reduction of alkene.

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10. Explain the reaction of alkynes with water.

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## • TEST YOURSELF

### Answers the following questions :

- How are alkanes prepared ? Describe their important reactions.
- Explain why alkanes are relatively unreactive.
- What happens when ethane reacts with chlorine ? Discuss its free radical mechanism.
- Write a note on Wurtz or Wurtz-Fittig reaction.
- Write a short note on reactivity and selectivity.
- What do you understand by elimination reactions ?
- Describe Saytzeff's rule with suitable example.
- Describe the preparation of 1-butene by Hofmann's elimination reaction.
- Describe Markownikov's rule and anti Markownikov's rule with examples.
- Explain ionic mechanism for electrophilic addition reaction.
- Describe the following reactions of alkenes ?
  - Oxymercuration and demercuration
  - Hydroboration reaction
  - Ozonolysis
  - Catalytic reduction
  - Oxidation reactions
- What are dienes ? Discuss the addition reactions with halogen and halogen acids with conjugate diene.
- Write a short note on alkylic substitution reaction.
- Explain the acidic nature of acetylene.
- Explain any two electrophilic addition reactions of alkynes.
- Describe hydration of alkynes.
- Which one of the following reactions can be used in the preparation of alkanes.
  - Wurtz's reaction
  - Wurtz-Fittig's reaction
  - Hofmann's reaction
  - All the above
- Ethylene reacts with HI to give
  - iodo ethane
  - 2, 2-Di iodo ethane
  - 1, 1-Di iodo ethane
  - Butane
- Acetylene reacts with water in the presence of sulphuric acid and mercuric sulphate to yield :
  - HCHO
  - CH<sub>3</sub>CHO
  - CH<sub>3</sub>COOH
  - HCOOH
- Baeyer's reagent is :
  - Dil. KMnO<sub>4</sub>
  - Acidic KMnO<sub>4</sub>
  - Alkaline KMnO<sub>4</sub>
  - All the above
- Choose the correct order of reactivity amongst the halogens ?
  - Cl > Br > I
  - I > Br > Cl
  - Br > Cl > I
  - Cl < Br > I
- Which one of the following reaction is most exothermic :
  - CH<sub>4</sub> + I<sub>2</sub> → CH<sub>3</sub> + HI
  - CH<sub>4</sub> + Br<sub>2</sub> → CH<sub>3</sub>Br + HBr
  - CH<sub>4</sub> + Cl<sub>2</sub> → CH<sub>3</sub>Cl + HCl
  - CH<sub>4</sub> + F<sub>2</sub> → CH<sub>3</sub>F + HF
- Propene on ozonolysis yields :
  - HCHO only
  - CH<sub>3</sub>CHO only
  - CH<sub>3</sub>CHO and HCHO
  - CH<sub>3</sub>CO.CH<sub>3</sub>
- Reactivity of hydrogen is more when attached to :
  - Primary carbon atom
  - Secondary carbon atom
  - Tertiary carbon atom
  - All the above
- When a solution of isopropyl bromide reacts with sodium in the presence of ether, the product formed is :

- (a) Hexane (b) Propane  
(c) Isopentene (d) 2, 3-Dimethyl butane
26. Alc. KOH is used for :  
(a) Dehydrogenation (b) Decarboxylation  
(c) Dehydrohalogenation (d) Dehydration
27. Which one of the following decolourises alk.  $\text{KMnO}_4$  :  
(a)  $\text{CH}_4$  (b)  $\text{C}_2\text{H}_4$  (c)  $\text{C}_2\text{H}_6$  (d)  $\text{C}_3\text{H}_8$
28. Following compound can be prepared by the hydroboration of alkene :  
(a) Alkane (b) Alkyne (c) Alcohol (d) Aldehyde
29. Fill in the blanks :  
(i) Alkanes mainly show ..... reactions.  
(ii) The molecular formula of heptane is .....  
(iii) Butene gives ..... test with Baeyer's reagent.  
(iv) Ozonolysis of ethene gives ..... glyoxal.  
(v) The addition of HBr on an unsymmetrical alkene takes place according to .....
30. Identify True (T) and False (F) Statements :  
(i) Wurtz reaction is used for the formation of methane.  
(ii) Wurtz-Fittig's reaction is used for the preparation of ethyl benzene.  
(iii) In alkanes C—C bond is stronger than C—H bond.  
(iv) Alkaline  $\text{KMnO}_4$  can be used for the identification of ethane and ethene.  
(v) Acetylene reacts with water in the presence of  $\text{H}_2\text{SO}_4$  only.

### ANSWERS

17. (a) 18. (a) 19. (b) 20. (c) 21. (a) 22. (d) 23. (c) 24. (c) 25. (d) 26. (c) 27. (b) 28. (c)  
29. (i) substitution, (ii)  $\text{C}_7\text{H}_{16}$ , (iii) positive, (iv) formaldehyde, (v) Markownikov's rule. 30. (i) F, (ii)  
(iii) F, (iv) T, (v) F



# DIRECTORATE OF DISTANCE EDUCATION



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