

**Notes  
On  
CHEMISTRY  
(I- B. Tech. – II– Semester)**

**Submitted to**

**DEPARTMENT OF BASIC SCIENCE AND HUMANITIES**

**By**

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**(2018-19)**

# **JNTUH SYLLABUS ( R 18 REGULATION)**

## **CH102BS/CH202BS: CHEMISTRY**

**B.Tech. I Year I Sem-(CSE, EEE), II Sem-(CE, ME, ECE & EIE)      L T P C**

## **UNIT-I (MOT, CFT & BAND THEORY)**

### **Molecular orbital Theory (MOT):**

- Atomic and Molecular orbital's.
  - Linear Combination of Atomic Orbital's (LCAO).
  - Molecular orbital's of diatomic molecules.
  - Molecular orbital energy level diagrams of N<sub>2</sub>, O<sub>2</sub> and F<sub>2</sub> molecules.
  - $\pi$  molecular orbital's of butadiene and benzene.

### **Crystal Field Theory (CFT):**

- Salient Features of CFT
  - Crystal Field Splitting of transition metal ion d- orbitals in Tetrahedral, Octahedral and square planar geometries.

## **Band structure of solids:**

- Band structure of solids
  - Effect of doping on conductance.

## **UNIT-II (WATER AND ITS TREATMENT)**

- Introduction – hardness of water
  - Causes of hardness
  - Types of hardness: temporary and permanent
  - Expression and units of hardness
  - Estimation of hardness of water by complexometric method.
  - Potable water and its specifications.
  - Steps involved in treatment of water – Disinfection of water by chlorination and ozonization.
  - Boiler feed water and its treatment – Calgon conditioning, Phosphate conditioning and Colloidal conditioning.
  - External treatment of water – Ion exchange process.
  - Desalination of water – Reverse osmosis.
  - Numerical problems.

### **UNIT-III (ELECTROCHEMISTRY, BATTERIES AND CORROSION)**

#### **Electrochemistry:**

- Electro chemical cells.
- Electrode potential, standard electrode potential.
- Types of electrodes – calomel, Quinhydrone and glass electrode.
- Nernst equation
- Determination of pH of a solution by using quinhydrone and glass electrode.
- Electrochemical series and its applications.
- Numerical problems.
- Potentiometric titrations.

#### **Batteries:**

- Primary (Lithium cell)
- Secondary batteries (Lead – acid storage battery and Lithium ion battery).

#### **Corrosion and its control:**

- Causes and effects of corrosion.
- Theories of chemical and electrochemical corrosion.
- Mechanism of electrochemical corrosion.
- Types of corrosion: Galvanic, water-line and pitting corrosion.
- Factors affecting rate of corrosion.
- Corrosion control methods- Cathodic protection– Sacrificial anode and Impressed current cathodic methods.
- Surface coatings – metallic coatings – methods of application.
- Electroless plating of Nickel.

### **UNIT-IV (STEREOCHEMISTRY, REACTION MECHANISM AND SYNTHESIS OF DRUG MOLECULES)**

#### **Stereochemistry:**

- Introduction to representation of 3-dimensional structures.
- Structural and stereoisomers.
- Configurations, symmetry and chirality.
- Enantiomers, diastereomers, optical activity and Absolute configuration.
- Conformation analysis of n- butane.

#### **Reaction Mechanism:**

- **Substitution reactions:**

Nucleophilic substitution reactions: Mechanism of S<sub>N</sub>1, S<sub>N</sub>2 reactions.

- **Electrophilic and nucleophilic addition reactions:**  
Addition of HBr to propene. Markownikoff and anti Markownikoff's additions. Grignard additions on carbonyl compounds.
- **Elimination reactions:**  
Dehydro halogenation of alkylhalides. Saytzeff rule.
- **Oxidation reactions:**  
Oxidation of alcohols using KMnO<sub>4</sub> and chromic acid.
- **Reduction reactions:**  
Reduction of carbonyl compounds using LiAlH<sub>4</sub> & NaBH<sub>4</sub>. Hydroboration of olefins.

#### Synthesis of drug molecules:

- Structure, synthesis and pharmaceutical applications of Paracetamol and Aspirin.

### **UNIT-V (SPECTROSCOPIC TECHNIQUES AND APPLICATIONS)**

- Principles of spectroscopy,
- Selection rules and applications of electronic spectroscopy, vibrational and rotational spectroscopy.
- Basic concepts of Nuclear magnetic resonance Spectroscopy, chemical shift.
- Introduction to Magnetic resonance imaging.

### **SUGGESTED TEXT BOOKS**

1. Physical Chemistry, by P.W. Atkins
2. Engineering Chemistry by P.C.Jain & M.Jain; Dhanpat Rai Publishing Company (P) Ltd., New Delhi.
3. Fundamentals of Molecular Spectroscopy, by C.N. Banwell
4. Organic Chemistry: Structure and Function by K.P.C. Volhardt and N.E.Schore, 5<sup>th</sup> Edition.
5. University Chemistry, by B.M. Mahan, Pearson IV Edition.
6. Engineering Chemistry (NPTEL Web-book), by B.L. Tembe, Kamaluddin and M.S. Krishnan.

**MOLECULAR ORBITAL THEORY****INTRODUCTION:**

1. VBT fails to answer the certain questions:  
Why O<sub>2</sub> is paramagnetic in nature?  
Why He<sub>2</sub> molecule does not exist?
2. The MOT was developed to provide answers to more complex questions.
3. This also helps in predicting molecular properties like Bond order, Bond length, Stability and magnetic property.

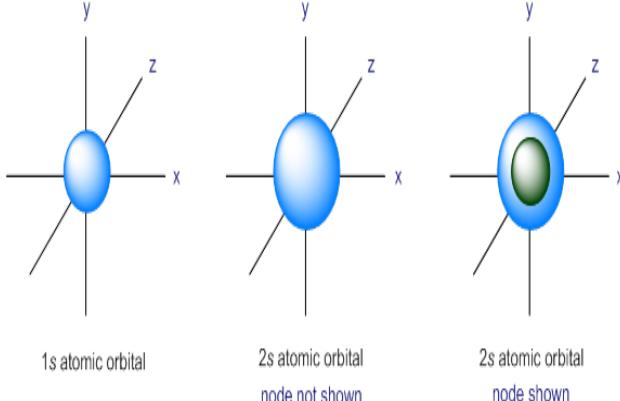
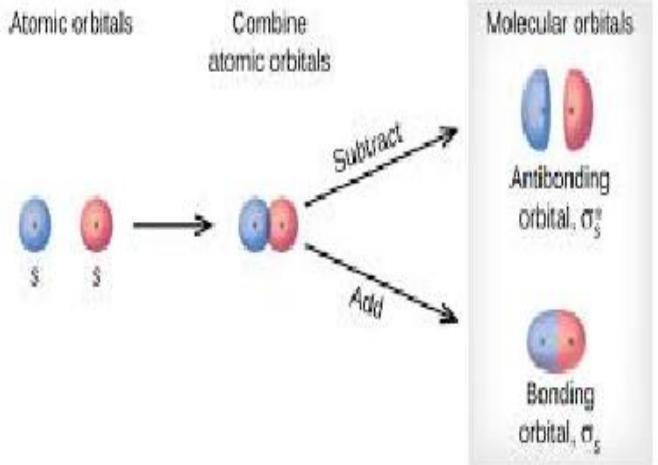
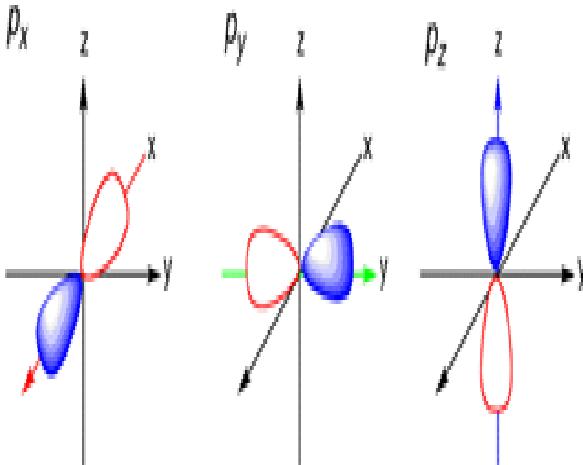
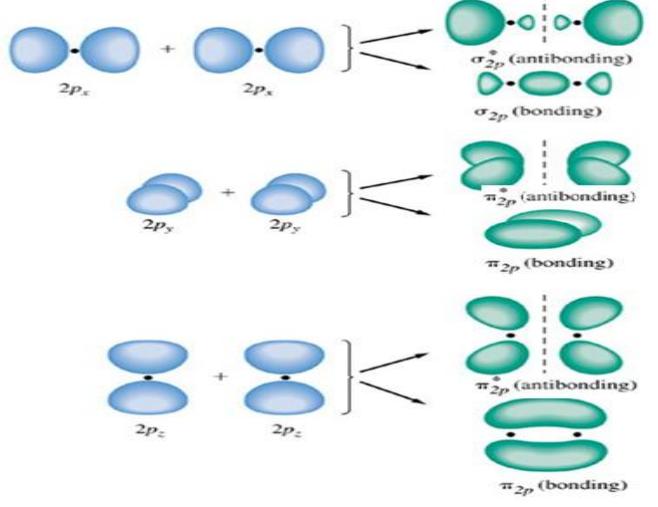
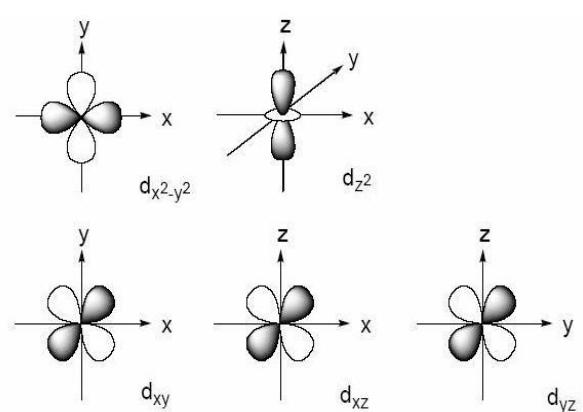
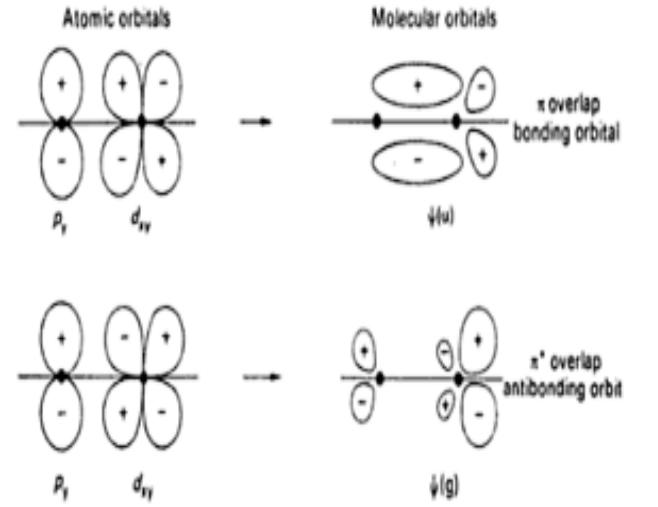
**SILENT FEATURES OF MOLECULAR ORBITAL THEORY**

1. The electrons in a molecule are present in various molecular orbitals as the electrons of atom are present in various atomic orbitals.
2. Atomic orbitals of comparable energies and proper symmetry combine to form molecular orbitals.
3. While an electron in an atomic orbital it is influenced by one nucleus, in a molecular orbital it is influenced by two (or) more nucleus depending upon the number of atoms in a molecule.
4. Atomic orbital is mono-centric and molecular orbital is poly-centric.
5. The number of molecular orbital formed is equal to the number of combining atomic orbitals.
6. When two atomic orbitals combine, two molecular orbitals are formed that are:
  - i. Bonding molecular orbital (BMO).
  - ii. Antibonding molecular orbital (ABMO).
7. Bonding molecular orbital (BMO) has lower energy and hence more stability than the corresponding Antibonding molecular orbital.
8. The electron probability distribution around a nucleous in an atom is given by an atomic orbital; the electron probability distribution around a group of nuclei in a molecule is given by molecular orbital.

**DIFFERENCE BETWEEN ATOMIC ORBITAL AND MOLECULAR ORBITAL**

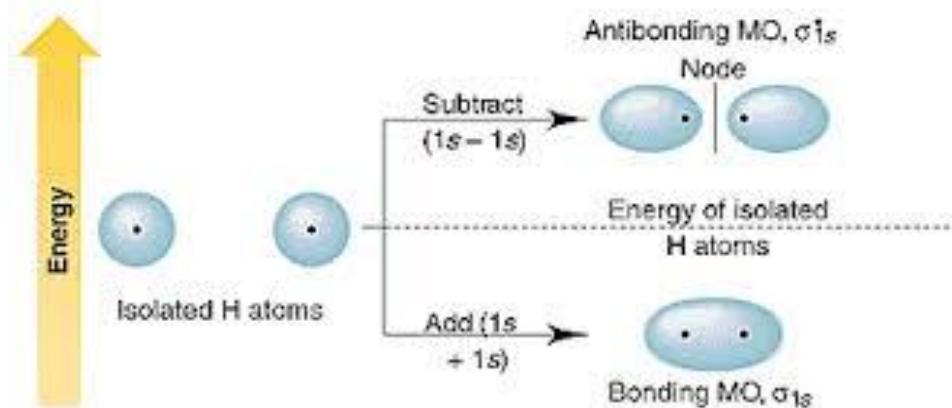
<b>ATOMIC ORBITAL</b>	<b>MOLECULAR ORBITAL</b>
1. Atomic orbital is the region having the highest probability of finding an electron in an atom.	Molecular orbital is the region having the highest probability of finding an electron of a molecule.
2. Atomic orbitals are formed by the electron cloud around the atom.	Molecular orbitals are formed by the fusion of atomic orbital's that have nearly the same energy.
3. The shape of atomic orbitals is determined by the type of the atomic orbital (s, p, d or f).	The shape of the molecular orbital is determined the shapes of atomic orbitals that make the molecule.
4. Schrodinger equation is used.	Linear combination of atomic orbital's (LCAO) is used.
5. Atomic orbital is mono centric as it is found around a single nucleus.	Molecular orbital is polycentric as it is found around different nuclei.

# UNIT-I

<p>6. Single nucleus affects the electron cloud in atomic orbital's</p> 	<p>Two more nuclei affect the electron cloud in molecular orbitals.</p> 
	
	

### LINEAR COMBINATION OF ATOMIC ORBITALS

- Atomic orbitals can be expressed by wave function ( $\psi$ ) which represents the amplitude of the electron waves.
  - These are obtained from the solution of Schrodinger wave equation, but this cannot be solved for the system with more than one electron.
  - So, molecular orbital cannot be obtained from Schrodinger wave equation, to overcome this problem an approximate method known as linear combination of atomic orbitals(LCAO) has been adopted.
  - Consider the hydrogen molecule consisting of two atoms A and B. Each hydrogen atom in the ground state has one electron in 1S orbital.
  - The atomic orbitals of these atoms may be represented by the wave functions  $\psi_A$  and  $\psi_B$ .
- $\Psi_{MO} = \psi_A \pm \psi_B$
- $\sigma = \psi_A + \psi_B$  (**bonding molecular orbitals**)
- $\sigma^* = \psi_A - \psi_B$  (**antibonding molecular orbitals**)
- The molecular orbitals( $\sigma$ ) formed by the addition of atomic orbitals is called the **bonding molecular orbitals** while the molecular orbitals( $\sigma^*$ ) formed by the subtraction of atomic orbitals is called **antibonding molecular orbitals**.



- Electron density in a bonding molecular orbital is located between the nuclei of the bonded atoms because of which the repulsion between the nuclei is very less while in the case of an antibonding Molecular Orbital, most of the electron density is located away from the space between the nuclei, hence the repulsion between the nuclei is high.
- Electrons placed in a bonding molecular orbital tend to hold the nuclei together and stabilize a molecule. Therefore, a bonding molecular orbital always possesses lower energy than either of atomic orbitals that have combined to form it.

- Electrons placed in the antibonding molecular orbital destabilizes the molecule. This is because the mutual repulsion of the electrons in this orbital is more than the attraction between the electrons in the nuclei, which causes a net increase in energy.
- The total energy of two molecular orbitals, however, remains the same as that of two original atomic orbitals.

## CONDITIONS FOR LINEAR COMBINATION OF ATOMIC ORBITALS (LCAO)

1. **Same energy of combining orbitals:** The combining atomic orbitals must have same or nearly same energy.  
**Eg:** This means that 2p orbital of an atom can combine with another 2p orbital of another atom but 1S and 2p cannot combine together as they have appreciable energy difference.
2. **Same symmetry about the molecular axis:** The combining atoms should have same symmetry around the molecular axis for proper combination.  
**Eg:** All the sub-orbitals of 2p have same energy but still, the  $2p_z$  orbital of an atom can only combine with a  $2p_z$  orbital of another atom but cannot combine with  $2p_x$  and  $2p_y$  orbital as they have a different Axis of symmetry (the z-axis is considered as the molecular axis of symmetry).
3. **Proper overlap between the atomic orbitals:** The two atomic orbitals will combine to form molecular orbital if the overlap is proper. Greater the extent of overlap of orbitals, greater will be the nuclear density between the nuclei of the two atoms.

## RULES FOR FILLING MOLECULAR ORBITAL ENERGY DIAGRAMS

### Aufbau Rule: (lower energy orbitals fill before higher energy orbitals):

This principle states that in the ground state of an atom or ion, electrons fill atomic orbitals of the lowest available energy levels before occupying higher levels. In this way, the electrons of an atom or ion form the most stable electron configuration possible.

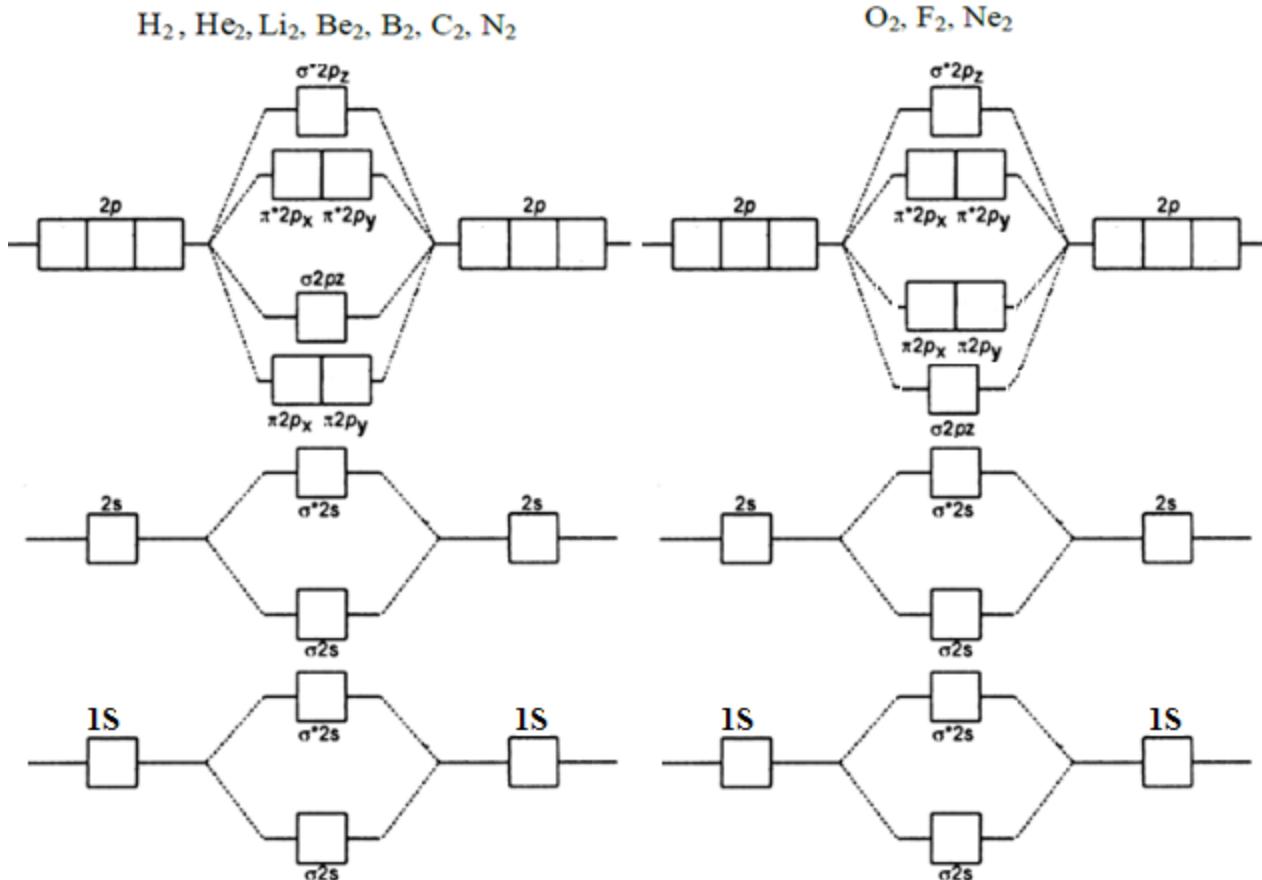
### Hund's Rule: (one electron goes into each until all of them are half full before pairing up):

In Hund's rule every orbital in a subshell is singly occupied with one electron before any one orbital is doubly occupied, and all electrons in singly occupied orbitals have the same spin.

### Pauli Exclusion Principle: (No two electrons can be identified by the same set of quantum numbers):

This principle states that no two electrons can be identified by the same set of quantum numbers. This is actually why we have the spin quantum number,  $m_s$ , to ensure that two electrons within the same orbital have unique sets of quantum numbers.

### ENERGY LEVEL DIAGRAM OF MOLECULAR ORBITAL FOR SIMPLE DIATOMIC MOLECULES



- The order of energy levels of the Homonuclear Molecular Orbitals(14 – electrons and below) in the order of increasing energy as follows:

$$\sigma(1\text{S}) < \sigma^*(1\text{S}) < \sigma(2\text{S}) < \sigma^*(2\text{S}) < \pi(2p_x = 2p_y) < \sigma(2p_z) < \pi(2p_x^* = 2p_y^*) < \sigma(2p_z^*)$$

- The order of energy levels of the Homonuclear Molecular Orbitals(14 – electrons above) in the order of increasing energy as follows:

$$\sigma(1\text{S}) < \sigma^*(1\text{S}) < \sigma(2\text{S}) < \sigma^*(2\text{S}) < \sigma(2p_z) < \pi(2p_x = 2p_y) < \pi(2p_x^* = 2p_y^*) < \sigma(2p_z^*)$$

**MOLECULAR ORBITAL DIAGRAMS FOR DIATOMIC MOLECULES**

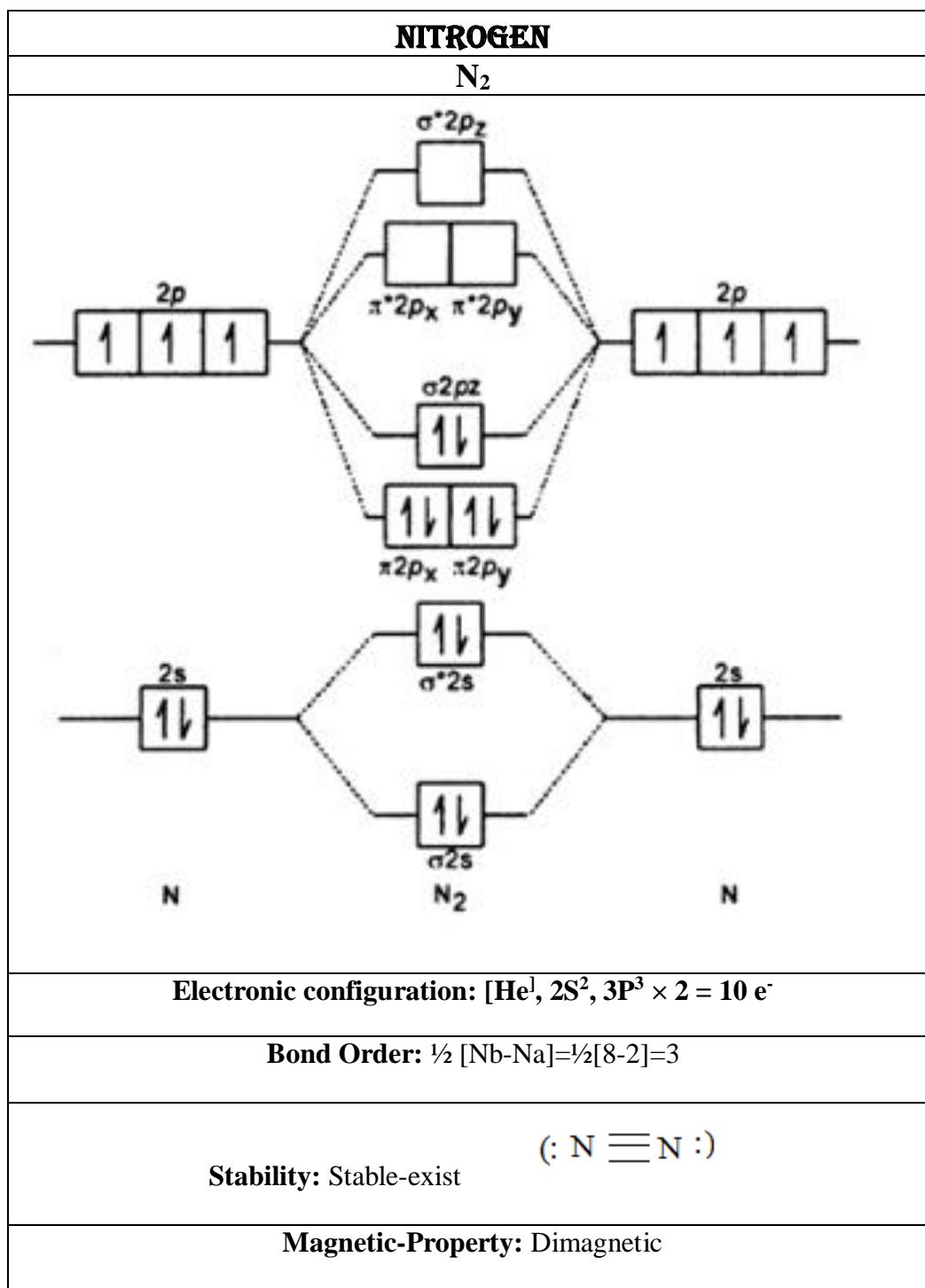
<b>HYDROGEN</b>		
<b>H<sub>2</sub></b>	<b>H<sub>2</sub><sup>+</sup></b>	<b>H<sub>2</sub><sup>-</sup></b>
<b>Bond Order:</b> $\frac{1}{2} [Nb-Na] = \frac{1}{2}[2-0] = 1$	<b>Bond Order:</b> $\frac{1}{2} [Nb-Na] = \frac{1}{2}[1-0] = \frac{1}{2}$	<b>Bond Order:</b> $\frac{1}{2} [Nb-Na] = \frac{1}{2}[2-1] = \frac{1}{2}$
<b>Stability:</b> Stable - exist	<b>Stability:</b> Stable - exist	<b>Stability:</b> Stable - exist
<b>Magnetic Property:</b> Diamagnetic	<b>Magnetic-Property:</b> Paramagnetic	<b>Magnetic-Property:</b> Paramagnetic

<b>HELIUM</b>	
, He <sub>2</sub> , 1s	He <sub>2</sub> <sup>+</sup>
<b>Bond Order:</b> $\frac{1}{2} [Nb-Na] = \frac{1}{2}[2-2] = 0$	<b>Bond Order:</b> $[Nb-Na] = \frac{1}{2}[2-1] = \frac{1}{2}$
<b>Stability:</b> Not exist	<b>Stability:</b> Stable - exist
<b>Magnetic-Property:</b> Diamagnetic	<b>Magnetic-Property:</b> Paramagnetic

LITHIUM $\text{Li}_2$	BERYLLIUM $\text{Be}_2$
<b>Electronic configuration:</b> $1S^2, 2S^1 \times 2 = 6 e^-$	<b>Electronic configuration:</b> $1S^2, 2S^2 \times 2 = 8 e^-$
<b>Bond Order:</b> $\frac{1}{2} [\text{Nb-Na}] = \frac{1}{2}[4-2] = 1$	<b>Bond Order:</b> $\frac{1}{2} [\text{Nb-Na}] = \frac{1}{2}[4-4] = 0$
<b>Stability:</b> Stable-exist (in the gas phase)	<b>Stability:</b> Not-exist
<b>Magnetic-Property:</b> Diamagnetic	<b>Magnetic-Property:</b> Diamagnetic
BORON $\text{B}_2$	CARBON $\text{C}_2$
<b>Electronic configuration:</b> $1S^2, 2S^2, 3P^1 \times 2 = 10 e^-$	<b>Electronic configuration:</b> $1S^2, 2S^2, 3P^2 \times 2 = 12 e^-$
<b>Bond Order:</b> $\frac{1}{2} [\text{Nb-Na}] = \frac{1}{2}[6-4] = 1$	<b>Bond Order:</b> $\frac{1}{2} [\text{Nb-Na}] = \frac{1}{2}[6-2] = 2$
<b>Stability:</b> Stable-exist	<b>Stability:</b> Stable-exist ( $\text{:C=C:}$ )
<b>Magnetic-Property:</b> Paramagnetic	<b>Magnetic-Property:</b> Diamagnetic

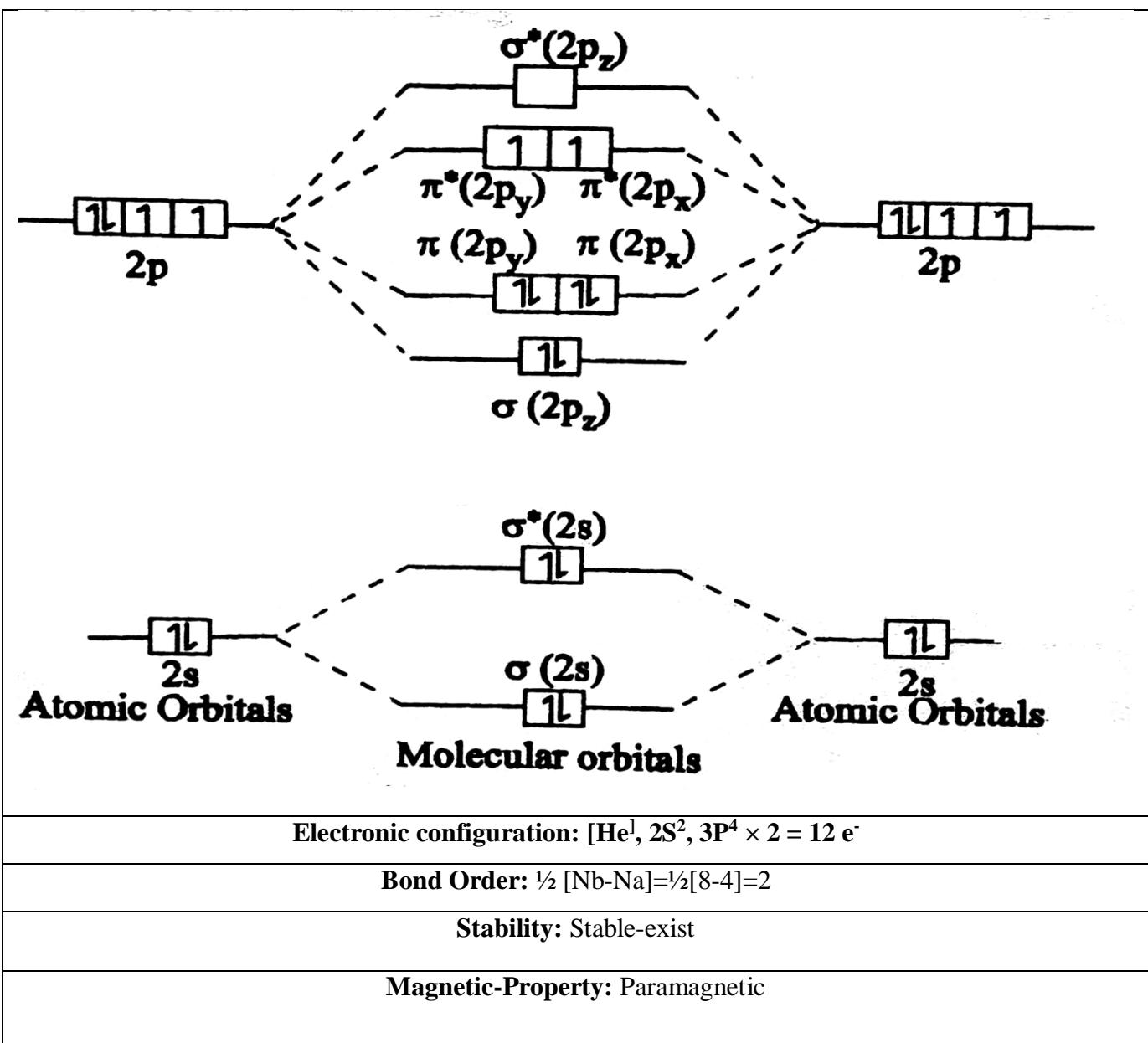
**MOLECULAR ORBITAL ENERGY DIAGRAMS OF NITROGEN**

Using Lewis structures, we predict a triple bond. MO theory also predicts 3 bonds, which match the experimental very short strong bond. Notice that in MO theory, the "lone pairs" (the 2 mostly non-bonding  $\sigma$  MOs) are shared over both atoms, and have different energies.



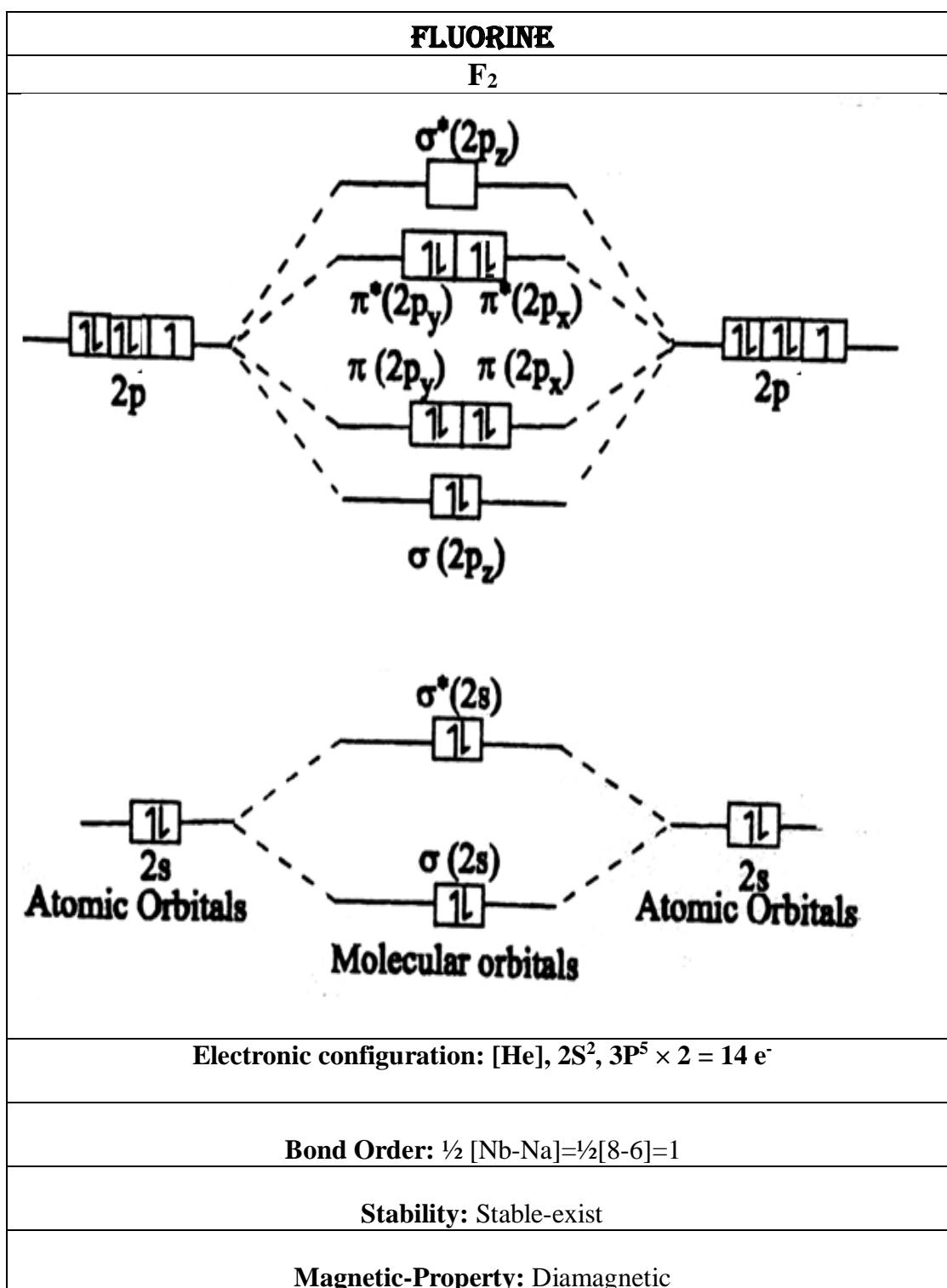
### MOLECULAR ORBITAL ENERGY DIAGRAMS OF OXYGEN

Using Lewis structures, we predict 2 bonds and no unpaired electrons. MO theory also predicts 2 bonds, but correctly predicts 2 unpaired electrons. This is a longer and weaker bond than in N<sub>2</sub> as we would expect. If we reduce O<sub>2</sub> by adding electrons, they go into the  $\pi^*$  orbitals, and make the bond weaker; this matches experiments showing that peroxide has a longer, weaker bond than O<sub>2</sub>.



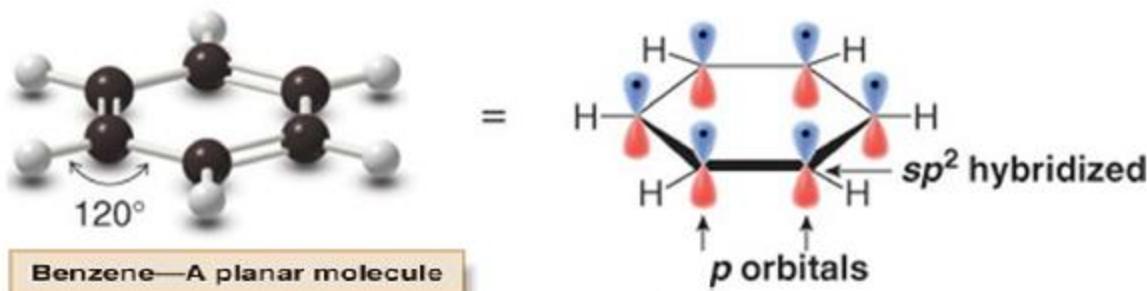
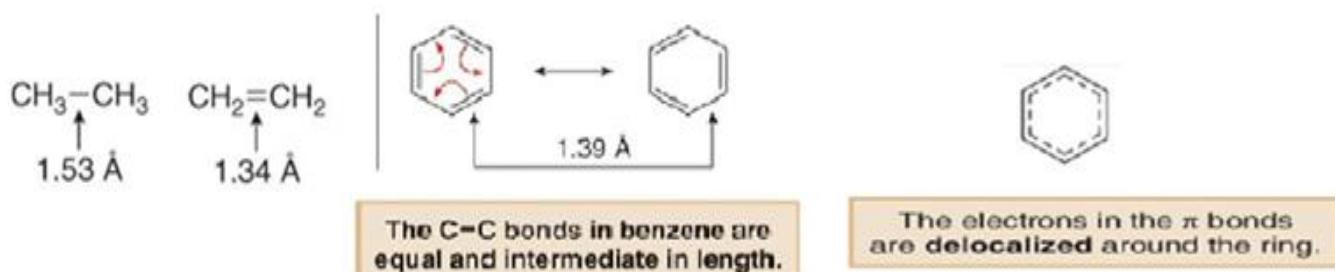
**MOLECULAR ORBITAL ENERGY DIAGRAMS OF FLUORINE**

Using Lewis structures, we predict 1 bond. MO theory also predicts 1 bond. This matches experiments showing a long, weak bond.



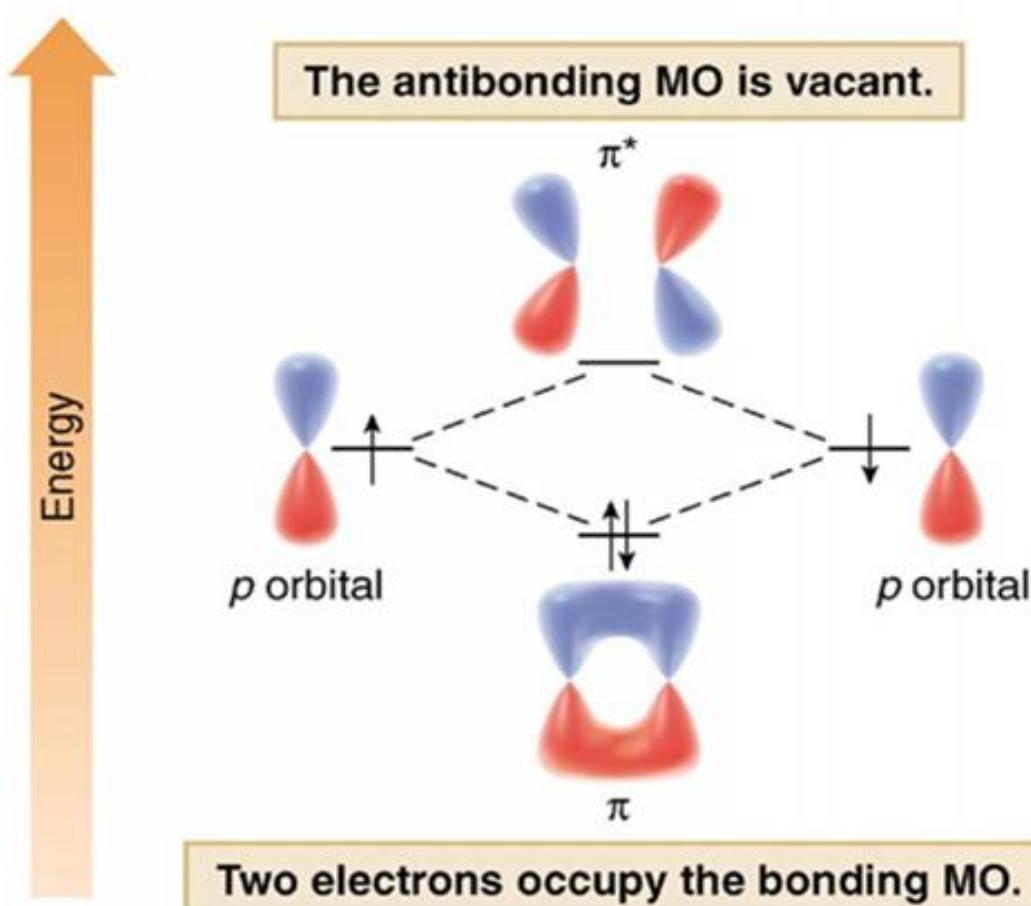
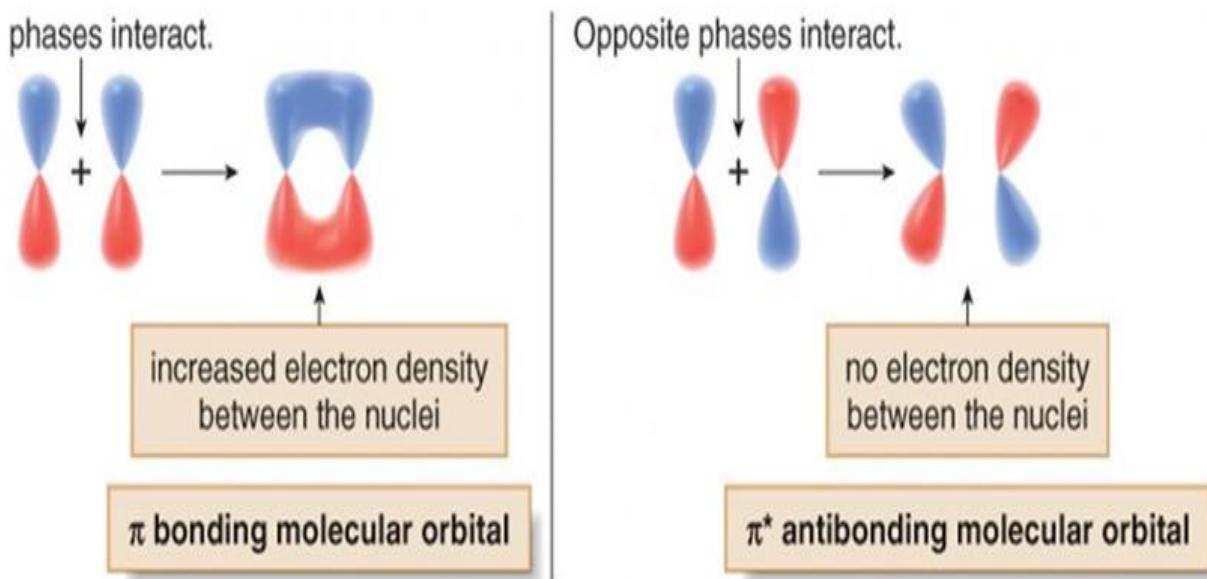
## $\pi$ MOLECULAR ORBITAL'S OF BENZENE

- Benzene consists of two equivalent Lewis structures, each with three double bonds that alternate with three single bonds, it is planar.
- In benzene, the actual bond length ( $1.39 \text{ \AA}$ ) is intermediate between the carbon—carbon single bond ( $1.53 \text{ \AA}$ ) and the carbon—carbon double bond ( $1.34 \text{ \AA}$ ). All C—C bond lengths are equal.



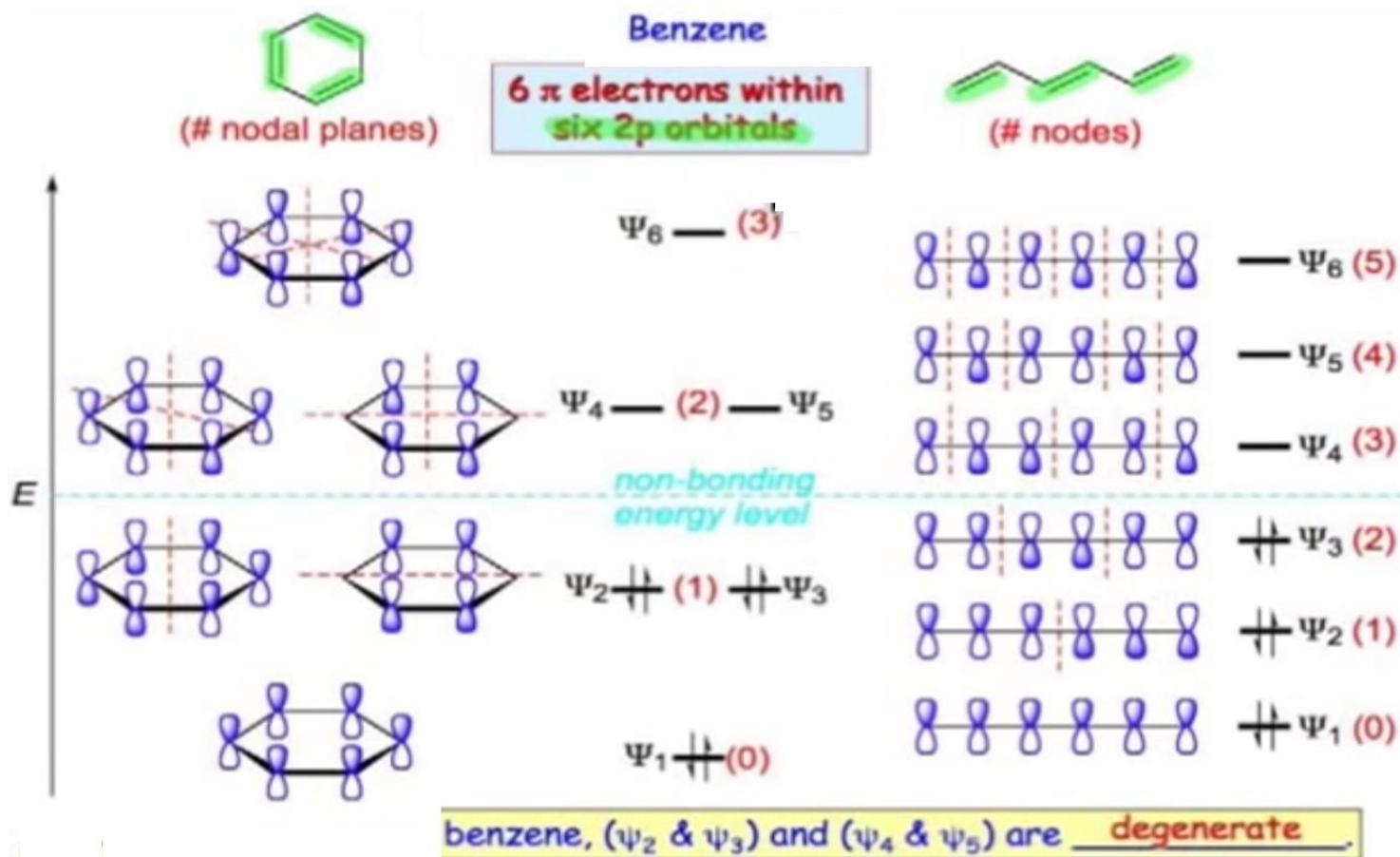
- Molecular orbital theory describes bonds as the mathematical combination of atomic orbitals that form a new set of orbitals called molecular orbitals (MOs).
- A molecular orbital occupies a region of space in a molecule where electrons are likely to be found.
- The combination of two  $p$  orbitals can be:
  - CONSTRUCTIVE** (with like phases interacting).
  - DESTRUCTIVE** (with opposite phases interacting).

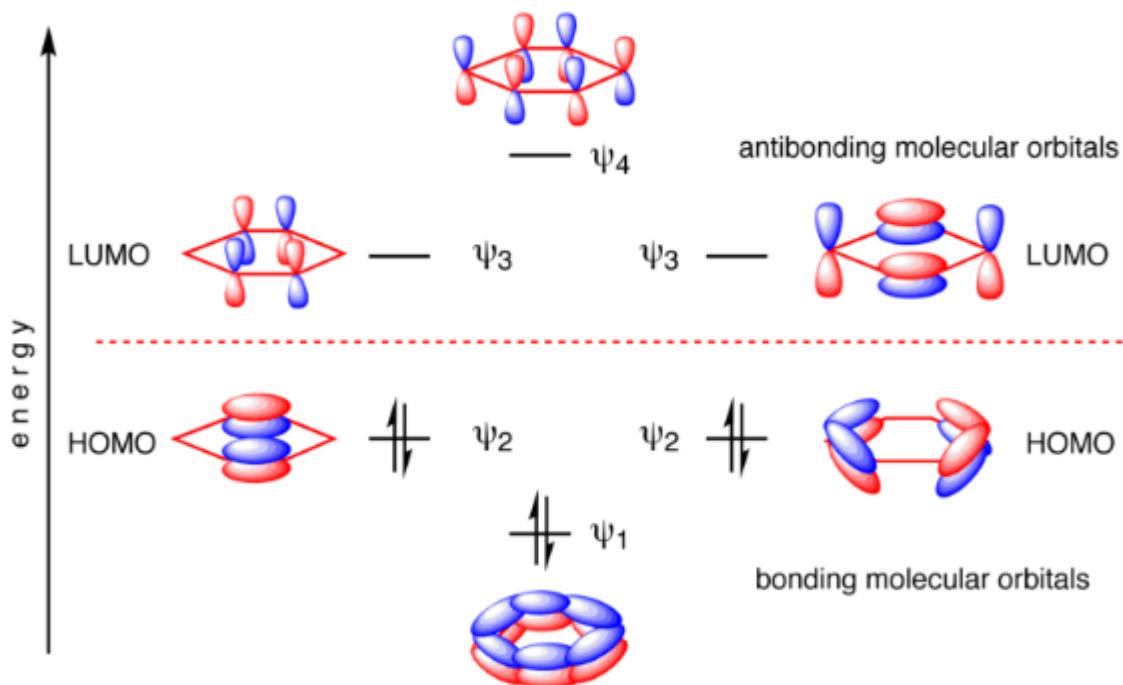
- Consider benzene. Since each of the six carbon atoms in benzene has a  $p$  orbital, six atomic  $p$  orbitals combine to form six molecular orbitals (MOs).



**MOST IMPORTANT FEATURES OF THE SIX BENZENE MOLECULAR ORBITALS:**

- The larger the number of bonding interactions, the lower in energy the molecular orbitals.
- The larger the number of nodes, the higher in energy the molecular orbitals.
- Three molecular orbitals are lower in energy than the starting *p* orbitals, making them **Bonding Molecular Orbitals**.
- Whereas three molecular orbitals are higher in energy than the starting *p* orbitals, making them **Anti Bonding Molecular Orbitals**.
- Two pairs of molecular orbitals with the same energy are called **Degenerate Orbitals**.
- The highest energy orbital that contains electrons is called the **Highest Occupied Molecular Orbital (HOMO)**.
- The lowest energy orbital that does not contain electrons is called the **Lowest Unoccupied Molecular Orbitals (LUMO)**.

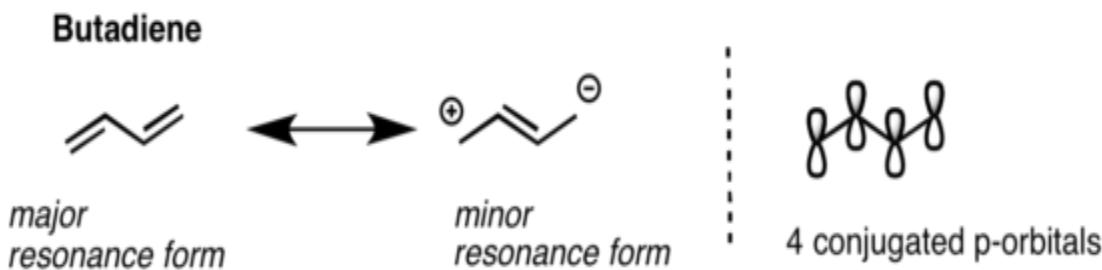




the  $\pi$  molecular orbitals for benzene. The dashed line represents the energy of an isolated p orbital – all orbitals below this line are bonding, all above it are antibonding. Benzene has six electrons in its  $\pi$  system so all the bonding MOs are fully occupied

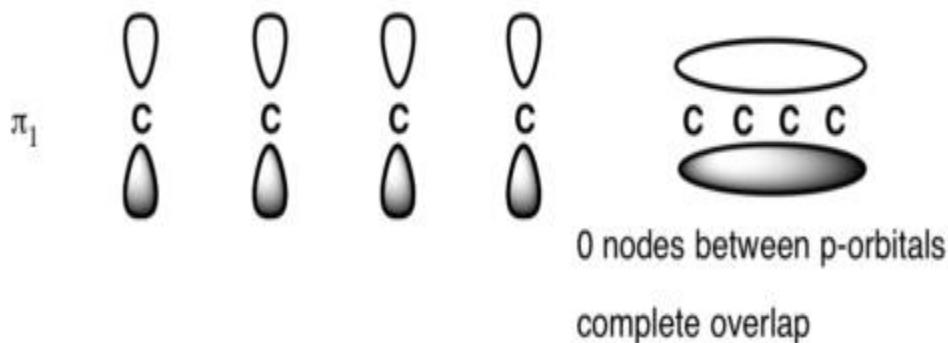
### $\pi$ MOLECULAR ORBITAL'S OF 1,3-BUTADIENE

- As the name suggests, 1,3-butadiene is composed of 4 carbons with two adjacent pi bonds.
- In these two pi bonds are conjugated, all four p orbitals are all aligned with each other, and build up into a larger pi system.
- It's for this reason that we can describe the electron density in butadiene with resonance forms.
- Since butadiene consists of 4 individual p orbitals, the pi-system of butadiene will contain 4 pi molecular orbitals.



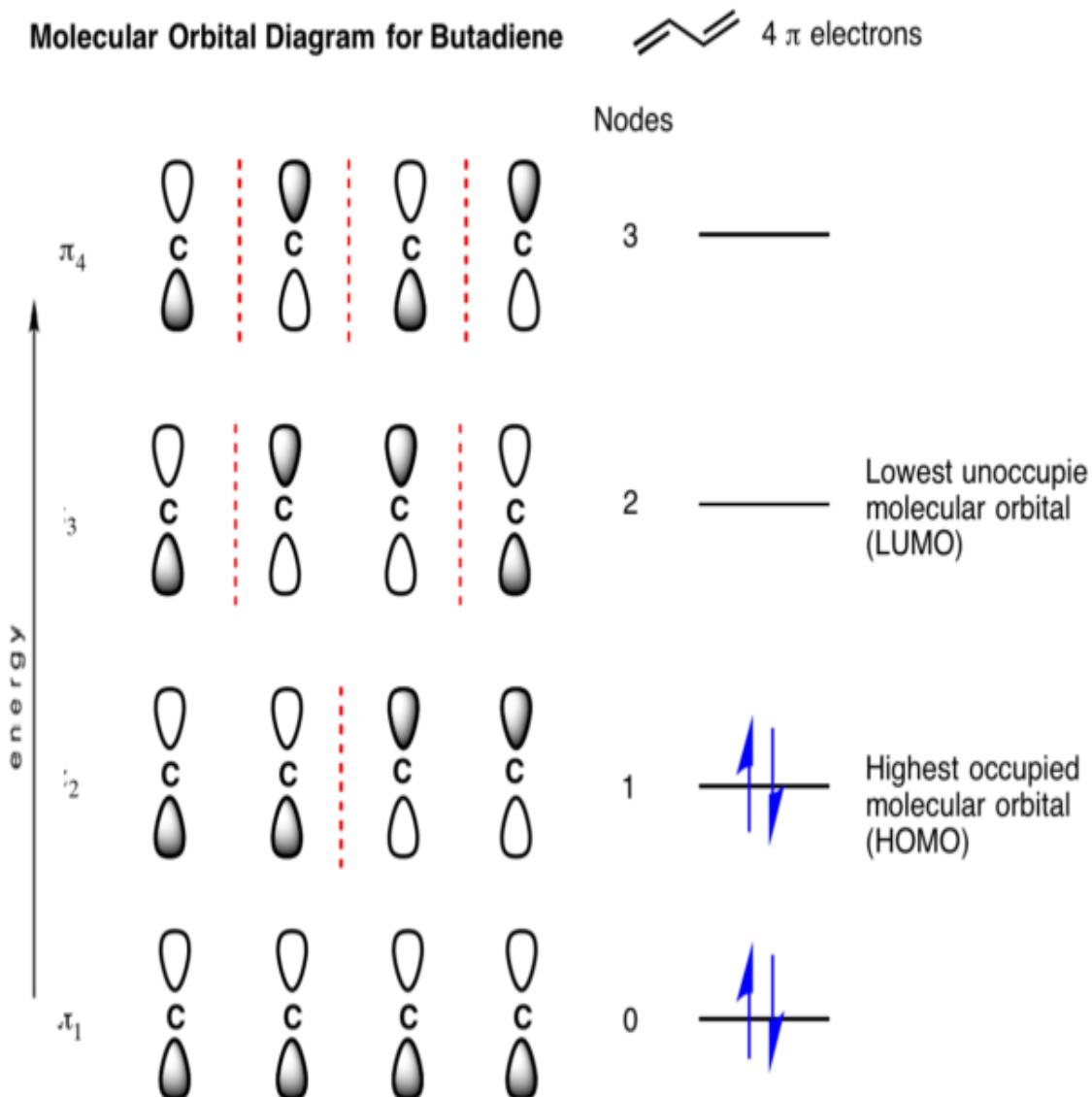
**Lowest-Energy Molecular Orbital ( $\pi_1$ ):**

- The lowest energy molecular orbital will have p orbitals with phases in complete alignment with each other and form **four Consecutive P-Orbitals** all aligned the same way.
- We could have also drawn the pi-system with all the shaded lobes pointing up.
- The constructive overlap between the lobes results in a pi orbital that extends over the entire length of the pi system (above right).
- There are **zero nodes** between the p orbitals themselves.
- A physical interpretation of this orbital is that an electron in this orbital is delocalized over the length of the pi system.

**Lowest-energy pi orbital in the butadienyl system has zero nodes****The Highest-Energy Molecular Orbital ( $\pi_4$ ):**

- The highest energy molecular orbital will have p orbitals with phases incomplete alignment with each other and form **four Destructive P-Orbitals**.
- Destructive overlap between the lobes results in a pi orbital that extends over the entire length of the pi system (above right).
- There are **nodes** between the p orbitals themselves.
- A physical interpretation of this orbital is that an electron in this orbital is delocalized over the length of the pi system Just draw n (4 in our case) p orbitals and alternate the phases of each.

- The highest energy orbital that contains electrons is called the **Highest Occupied Molecular Orbital (HOMO)**.
- The lowest energy orbital that does not contain electrons is called the **Lowest Unoccupied Molecular Orbitals(LUMO)**.



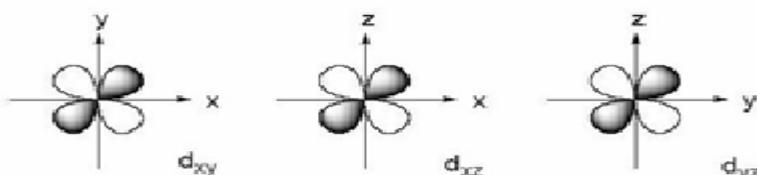
## CRYSTAL FIELD THEORY

### INTRODUCTION:

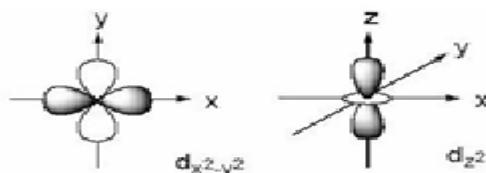
- a. **Crystal Field Theory** describes the breaking of degeneracy of electron orbital states of *d-orbitals*, due to a static electric field produced by a surrounding charge distribution (anion neighbors).
- b. CFT successfully accounts for magnetic properties, colors, Hydration enthalpies of transitional metal complexes.
- c. CFT was developed by physicists **BETHE** and **VAN VLECK** in the 1930's.

### SILENT FEATURES OF CRYSTAL FIELD THEORY

- i. The transition metal ion is surrounded by the ligands with lone pairs of electrons (The complex is a combination of central ion surrounded by the ligands like Anions (or) Neutral ions).
- ii. In ligands all type of anions regarded as point charges and Neutral ions as ion dipoles.
- iii. The interactions between the Metal ion and the ligand (anion (or) negative ends of ion dipoles) are purely electrostatic.
- iv. The ligands surrounding the metal ion produce electrical field and this electrical field influences the energies of the orbitals of central metal ion, particularly *d-orbitals*.
- v. In the case of free metal ion, all the five *d-orbitals* have the same energy. Such orbitals having the same energies are called *degenerate orbitals*.
- vi. These *degenerate d-orbitals* split into two sets with an energy difference.



*d<sub>xy</sub>, d<sub>xz</sub> and d<sub>yz</sub>* orbitals will be lower in energy(less repulsion) - referred to as t<sub>2g</sub>



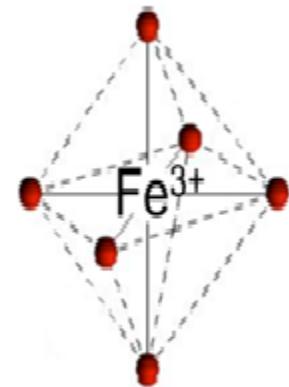
*d<sub>x^2-y^2</sub>* and *d<sub>z^2</sub>*, which will have higher energy(more repulsion) - referred to as e<sub>g</sub>.

**CRYSTAL FIELD SPLITTING OF TRANSITION METAL ION d-ORBITALS**

- According to crystal field theory, the interaction between a transition metal and ligands arises from the attraction between the positively charged metal cation and negative charge on the non-bonding electrons of the ligand.
- The theory is developed by considering energy changes of the five degenerate *d*-orbitals upon being surrounded by an array of point charges consisting of the ligands.
- As a ligand approaches the metal ion, the electrons from the ligand will be closer to some of the *d*-orbitals and farther away from others, causing a loss of degeneracy.
- The electrons in the *d*-orbitals and those in the ligand repel each other due to repulsion between like charges.
- Thus the *d*-electrons closer to the ligands will have a higher energy than those further away which results in the *d*-orbitals splitting in energy.

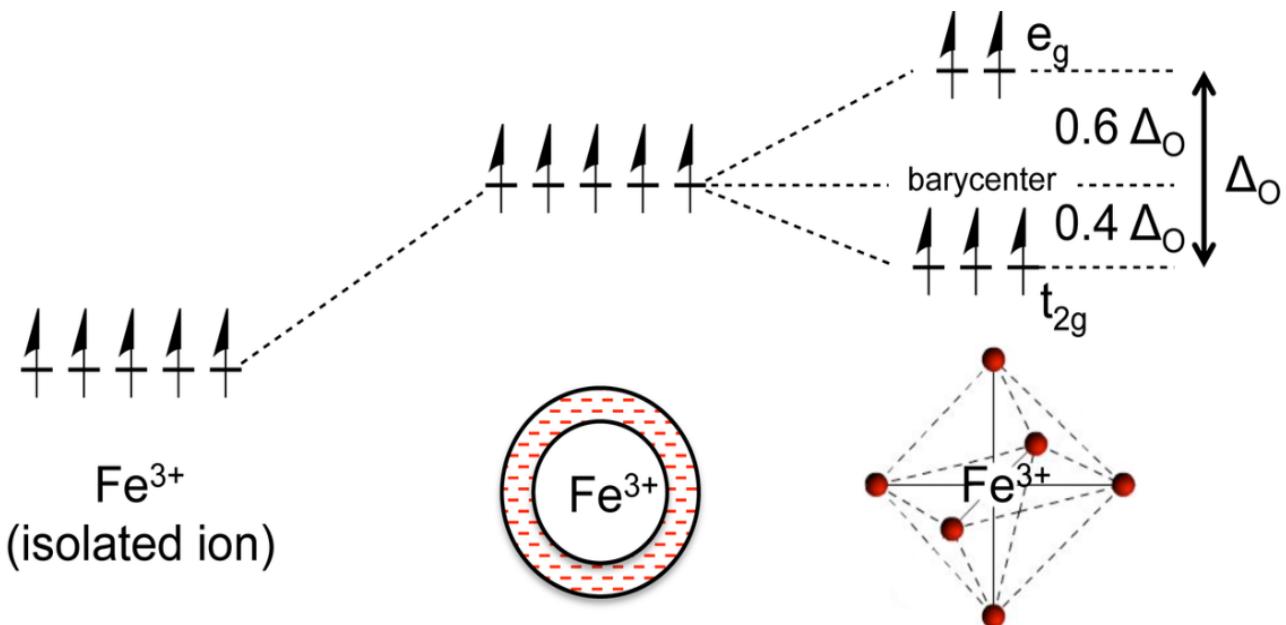
**CRYSTAL FIELD SPLITTING OF TRANSITION METAL ION d - ORBITALS IN OCTAHEDRAL GEOMETRY**

- In octahedral complex; here six ligands form an octahedron around the metal ion.
- In octahedral symmetry the *d*-orbitals split into two sets with an energy difference:
  - $d_{xy}$ ,  $d_{xz}$  and  $d_{yz}$  orbitals will be lower in energy(less repulsion).
  - $d_z^2$  and  $d_{x^2-y^2}$ , which will have higher energy(more repulsion).
- The three lower-energy orbitals are collectively referred to as  $t_{2g}$ , and the two higher-energy orbitals as  $e_g$ .
- In an octahedral complex, the  $d_z^2$  and  $d_{x^2-y^2}$  orbitals point directly at some of the ligand while the  $d_{xy}$ ,  $d_{xz}$  and  $d_{yz}$  orbitals are not.
- This enhances the repulsion between electrons in a metal  $d_z^2$  and  $d_{x^2-y^2}$  orbital and the donated electron pair from the ligand, raising the energy of these metal orbitals relative to the other three.
- The difference in energy between these two sets of *d*-orbitals is called the crystal field splitting  $\Delta$  or  $10 Dq$ , its magnitude depends on the metal and the nature of the ligands.
- The gain in energy by preferential filling up of orbitals by electrons is known as Crystal field stabilization energy (CFSE).



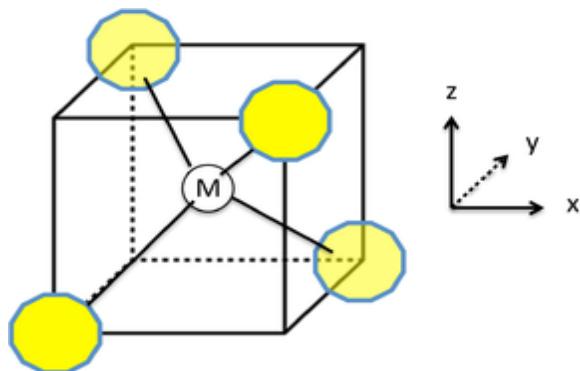
8. Greater the amount of CFSE of the complex, greater is the stability.

9. Example:  $[\text{Fe}(\text{CN})_6]^{3-}$  strong field ligand and low spin complex.



### CRYSTAL FIELD SPLITTING OF TRANSITION METAL ION d-ORBITALS IN TETRAHEDRAL GEOMETRY

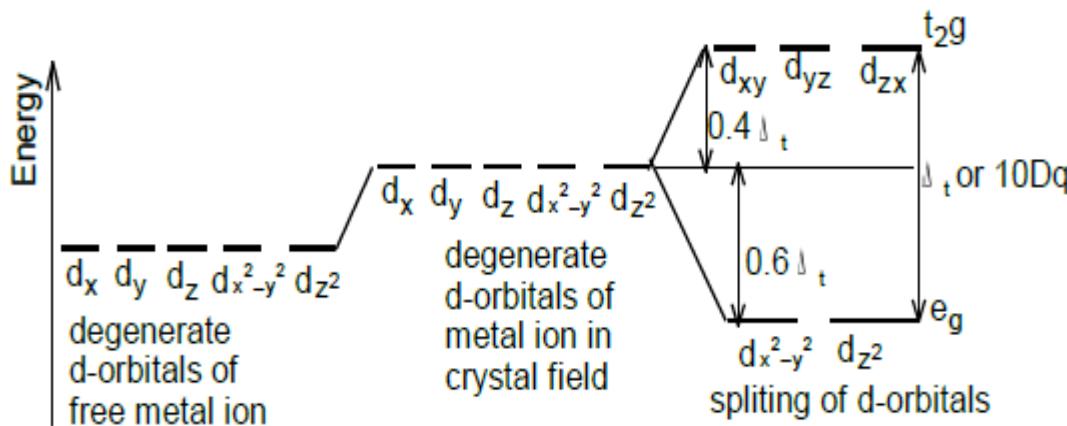
1. The splitting of the d-orbitals in a tetrahedral crystal field can be understood by connecting the vertices of a tetrahedron to form a cube, as shown in the picture:



2. The tetrahedral M-L bonds lie along the body diagonals of the cube. The  $d_{z^2}$  and  $d_{x^2-y^2}$  orbitals point along the axes, i.e., towards the faces of the cube, and have the least contact with the ligand lone pairs.
3. Therefore these two orbitals form a low energy, doubly degenerate ( $e_g$ ) set. The  $d_{xy}$ ,  $d_{yz}$ , and  $d_{zx}$  orbitals point at the edges of the cube and form a triply degenerate ( $t_{2g}$  set). While the

$t_{2g}$  orbitals have more overlap with the ligand orbitals than the  $eg$  set, they are still weakly interacting compared to the  $eg$  orbitals of an octahedral complex.

- The resulting crystal field energy diagram is shown at the right. The splitting energy,  $\Delta_t$ , is about 4/9 the splitting of an octahedral complex formed with the same ligands.
- For 3d elements,  $\Delta_t$  is thus small compared to the pairing energy and their tetrahedral complexes are always high spin.
- Note that we have dropped the "g" subscript (doubly degenerate -eg) set because the tetrahedron does not have a center of symmetry.



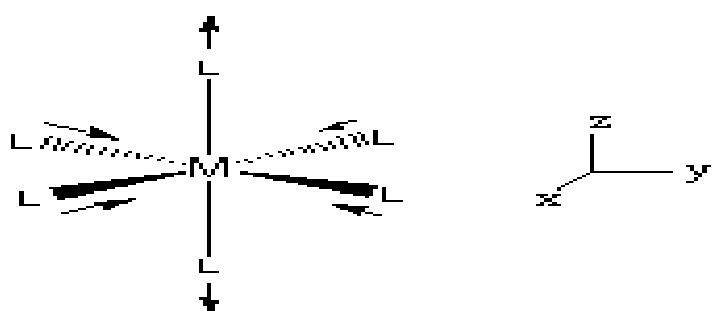
- Crystal field splitting of tetrahedral complex is lesser than that in octahedral complex is, due to less number of ligands(4-ligands), so the field is small and the direction of the orbitals does not coincide with that of ligands.
- Example:**  $[\text{CoCl}_4]^{2-}$  weak field ligand, high spin complex.

### CRYSTAL FIELD SPLITTING OF TRANSITION METAL ION d-ORBITALS IN SQUARE PLANAR GEOMETRY

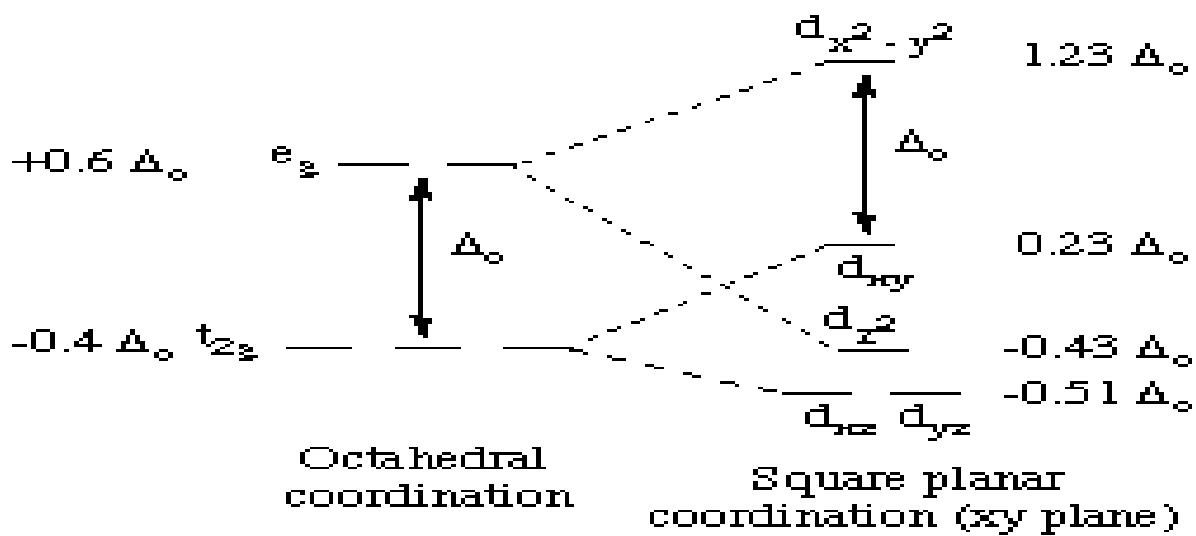
- The square planar geometry can then be considered as a deformation of the octahedral geometry, which will occur along the  $z$ -axis.

- The  $z$ -axis contains the two axial atoms

(top and bottom of the octahedron), so that four atoms stay in position and the symmetry. This will lift the degeneracy of most orbitals.



3. Square planar coordination can be imagined to result when two ligands on the z-axis of an octahedron are removed from the complex, leaving only the ligands in the x-y plane. As the z-ligands move away, the ligands in the square plane move a little closer to the metal.
4. The orbital splitting diagram for square planar coordination can thus be derived from the octahedral diagram. As ligands move away along the z-axis, d-orbitals with a z-component will fall in energy. The  $d_{z^2}$  orbital falls the most, as its electrons are concentrated in lobes along the z-axis. The  $d_{xz}$  and  $d_{yz}$  orbitals also drop in energy, but not as much. Conversely, the  $d_{x^2-y^2}$  and the  $d_{xy}$  orbitals increase in energy.



5. The splitting diagram for square planar complexes is more complex than for octahedral and tetrahedral complexes, and is shown below with the relative energies of each orbital.
6. The  $dx^2-y^2$  orbital will still be high in energy, but the orbital will be stabilised, because there are no more ligands in this direction. Due to the breaking of the octahedral symmetry, the three orbitals at the bottom of the octahedral diagram will no longer be degenerate. One of them - the one along the  $xy$  plane - will acquire a higher energy and the other two will be further stabilised.
7. **Example:**  $[\text{Ni}(\text{CN})_4]^{2-}$  strong field ligand and low spin complex.

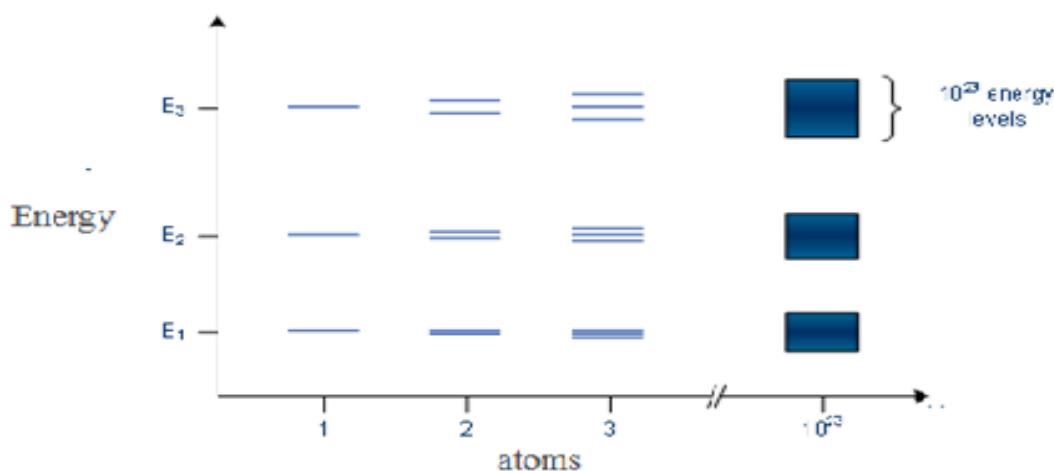
## BAND STRUCTURE OF SOLIDS

The electronic band structure is an energy schema to describe the conductivity of conductors, insulators, and semiconductors.

The schema consists of two energy bands (valence and conduction band) and the band gap. The valence electrons - which serve as charge carriers - are located in the valence band, in the ground state the conduction band is occupied with no electrons. Between the two energy bands there is the band gap; its width affects the conductivity of materials.

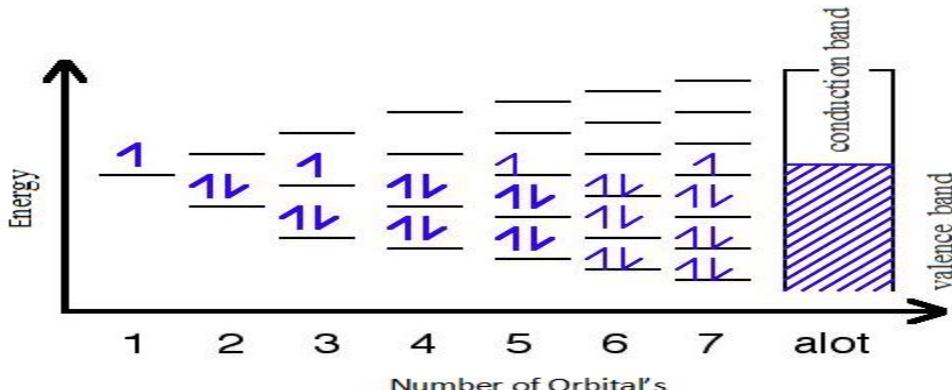
### The energy bands

If we consider a single atom, there are according to the Bohr model of atoms sharply distinct energy levels, which may be occupied by electrons. If there are multiple atoms side by side they are interdependent, the discrete energy levels are fanned out. In a silicon crystal, there are approximately  $10^{23}$  atoms per cubic centimeter, so that the individual energy levels are no longer distinguishable from each other and thus form broad energy ranges.



The width of the energy bands depends on how strongly the electrons are bound to the atom. The valence electrons in the highest energy level interact strongly with those of neighboring atoms and can be solved relatively easily from an atom; with a very large number of atoms, a single electron can no longer be assigned to one single atom. As a result, the energy bands of the individual atoms merge to a continuous band, the valence band. Bands - very closely spaced orbitals with not much difference in Energy. In this image, orbitals are represented by the black horizontal lines, and they are being filled with an increasing number of electrons as their amount increases. Eventually, as more orbitals are added, the space in between them decreases to hardly anything, and as a result, a band is formed where the orbitals have been filled.

Different metals will produce different combinations of filled and half filled bands.



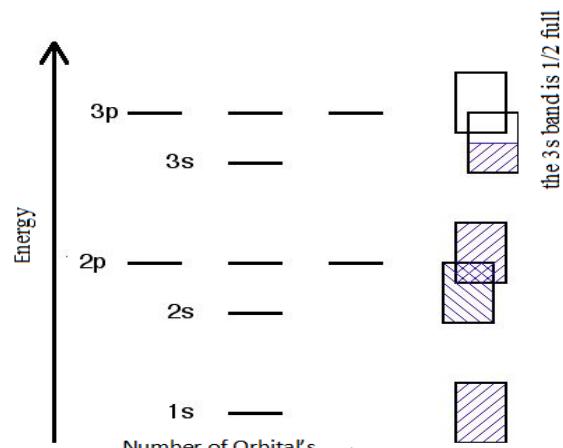
### Example:

Sodium's bands are shown with the rectangles.

Filled bands are colored in blue. As you can see, bands may overlap each other (the bands are shown askew to be able to tell the difference between different bands). The lowest unoccupied band is called the conduction band, and the highest occupied band is called the valence band.

Bands will follow a trend as you go across a period:

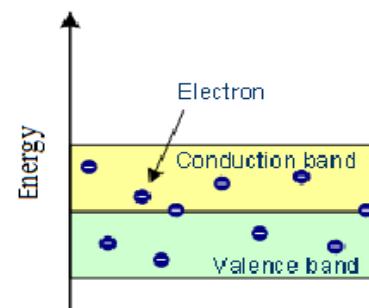
- In Na, the 3s band is 1/2 full.
- In Mg, the 3s band is full.
- In Al, the 3s band is full and the 3p band is 1/2 full... and so on.



## BAND STRUCTURE OF CONDUCTORS, SEMICONDUCTORS & INSULATORS

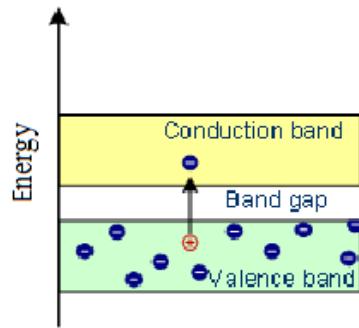
### The band model of conductors:

In conductors, the valence band is either not fully occupied with electrons, or the filled valence band overlaps with the empty conduction band. In general, both states occur at the same time, the electrons can therefore move inside the partially filled valence band or inside the two overlapping bands. In conductors there is no band gap between the valence band and conduction band.



### The band model of semiconductors:

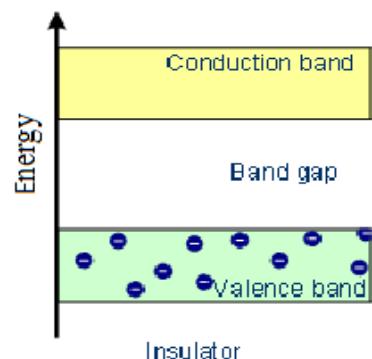
In semiconductors, band gap is so small that even at room temperature electrons from the valence band can be lifted into the conduction band. The electrons can move freely and act as charge carriers. In addition, each electron also leaves a hole in the valence band behind, which can be filled by other electrons in the valence band. Thus one gets wandering holes in the valence band, which can be viewed as positive charge carriers.



There are always pairs of electrons and holes, so that there are as many negative as positive charges, the semiconductor crystal as a whole is neutral. A pure undoped semiconductor is known as intrinsic semiconductor. Per cubic centimeter there are about  $10^{10}$  free electrons and holes (at room temperature).

### The band model of insulators:

In insulators the valence band is fully occupied with electrons due to the covalent bonds. The electrons cannot move because they're "locked up" between the atoms. To achieve conductivity, electrons from the valence band have to move into the conduction band. This prevents the band gap, which lies in-between the valence band and conduction band.



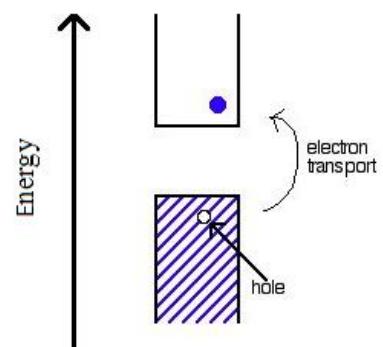
Only with considerable energy expenditure (if at all possible) the band gap can be overcome; thus leading to a negligible conductivity.

## DOPING IN SEMICONDUCTORS

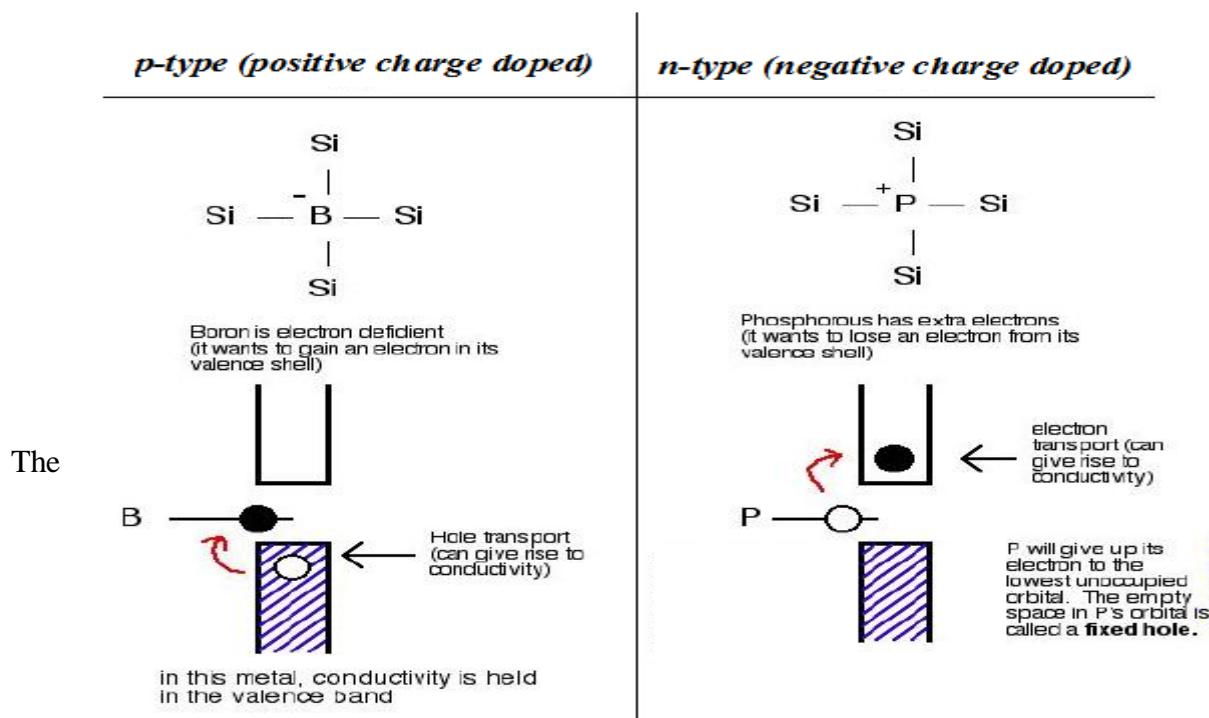
Semiconductors have a small energy gap between the valence band and the conduction band. Electrons can make the jump up to the conduction band, but not with the same ease as they do in conductors.

There are two different kinds of semiconductors:  
**intrinsic** and **extrinsic**.

- i. **Intrinsic Semiconductors:** An intrinsic semiconductor is a semiconductor in its pure state. For every electron that jumps into the conduction band, the missing electron will generate a hole that can move freely in the valence band. The number of holes will equal the number of electrons that have jumped.



**ii. Extrinsic Semiconductors:** In extrinsic semiconductors, the band gap is controlled by purposefully adding small impurities to the material. This process is called **doping**. Doping, or adding impurities to the lattice can change the electrical conductivity of the lattice and therefore vary the efficiency of the semiconductor. In extrinsic semiconductors, the number of holes will not equal the number of electrons jumped. There are two different kinds of extrinsic semiconductors, p-type (positive charge doped) and n-type (negative charge doped).



### PROBABILITY OF FINDING AN ELECTRON IN THE CONDUCTION BAND

Probability of finding an electron in the conduction band is shown by the equation:

$$P = \frac{1}{e^{\Delta E/RT} + 1}$$

$\Delta E$  stands for energy gap  
 $t$  stands for the temperature  
 $R$  is a bonding constant

Based on energy gap, between the valence band and the conduction band, the less likely electrons are to be found in the conduction band. This is because they cannot be excited enough to make the jump up to the conduction band.

**Ex:** In Carbon (diamond)  $\Delta E$ - energy gap is 524 kJ/mol and number of electrons per  $\text{cm}^3$  is  $10^{-27}$ , it is insulator.

In Si,  $\Delta E$ - energy gap is 117 kJ/mol and number of electrons per  $\text{cm}^3$  is  $10^9$ , it is semiconductor.

In Ge,  $\Delta E$ - energy gap is 66 kJ/mol and number of electrons per  $\text{cm}^3$  is  $10^{13}$ , it is semiconductor.

## ***Learning objectives:***

**After completion of this unit the student should be able to:**

- Atomic and Molecular orbital's.
- Linear Combination of Atomic Orbital's (LCAO).
- Molecular orbital's of diatomic molecules.
- Molecular orbital energy level diagrams of  $N_2$  molecule.
- Molecular orbital energy level diagrams of  $O_2$  molecule.
- Molecular orbital energy level diagrams of  $F_2$  molecule.
- $\pi$  molecular orbital's of butadiene.
- $\pi$  molecular orbital's of benzene.
- Salient Features of Crystal Field Theory.
- Crystal Field Splitting of transition metal ion d- orbitals in Tetrahedral geometry.
- Crystal Field Splitting of transition metal ion d- orbitals in Octahedral geometry.
- Crystal Field Splitting of transition metal ion d- orbitals in square planar geometry.

## ***Short Answer Questions:***

1. Distinguish between atomic and molecular orbitals.
2. Describe the atomic orbital diagrams of S, P(X, Y & Z) d-Orbital - $t_{2g}$  and  $e_g$ .
3. What is the bond order of  $N_2$  and  $O_2$  molecules?
4. Explain linear combination of atomic orbitals (LCAO) method.
5. What is the energy order of 14 and less than 14 electrons?
6. Explain  $\pi$  molecular energy level diagrams of butadiene.
7. What are the Salient Features of CFT.
8. Draw two sets of *degenerate orbitals* of d-orbitals.
9. Why Crystal field splitting of tetrahedral complex is lesser than that in octahedral complex?
10. Draw crystal Field splitting diagram of transition metal ion d- orbital's in square planar geometry.
11. Explain the band structure of conductors, semiconductors and insulators.
12. Explain effects of doping on conductance?

***Descriptive Questions:***

1. Explain Molecular energy level diagrams of N<sub>2</sub>.
2. Describe the Molecular energy level diagrams of O<sub>2</sub>.
3. Explain  $\pi$  molecular orbital's of benzene.
4. Describe crystal field splitting of transition metal ion d- orbitals in octahedral geometry.
5. What is crystal Field splitting of transition metal ion d- orbital's in tetrahedral geometry.
6. What is crystal Field splitting of transition metal ion d- orbital's in square planar geometry.
7. Explain doping in semi conductors.

***Objective Questions:***

1. Which of the following d-orbitals are in *Between the axis*? [ a ]
  - a. d<sub>xy</sub>, d<sub>xz</sub> and d<sub>yz</sub>
  - b. d<sub>z</sub><sup>2</sup> and d<sub>x<sup>2</sup>-y<sup>2</sup></sub>
  - c. d<sub>xz</sub> and d<sub>yz</sub>
  - d. d<sub>xy</sub>, and d<sub>xz</sub>
2. According to the molecular orbital theory magnetic nature of the *Fluorine* is. [ b ]
  - a. Paramagnetic
  - b. Diamagnetic
  - c. Ferromagnetic
  - d. Anti-ferromagnetic.
3. What is the coordination number of *octahedral geometry*? [ b ]
  - a. 4
  - b. 6
  - c. 5
  - d. 7
4. In which type of doping creates +ve holes in semiconductor. [ a ]
  - a. p-type
  - b. n-type
  - c. Both a & b
  - d. s-type
5. Which of the following d-orbitals are along the axis? [ b ]
  - a. d<sub>xy</sub>, d<sub>xz</sub> and d<sub>yz</sub>
  - b. d<sub>z</sub><sup>2</sup> and d<sub>x<sup>2</sup>-y<sup>2</sup></sub>
  - c. d<sub>xz</sub> and d<sub>yz</sub>
  - d. d<sub>xy</sub>, and d<sub>xz</sub>
6. According to the molecular orbital theory magnetic nature of the *Nitrogen* is. [ b ]
  - a. Paramagnetic
  - b. Diamagnetic
  - c. Ferromagnetic
  - d. Anti-ferromagnetic.
7. According to the crystal field theory what is the force between metal and ligand. [ a ]
  - a. Electrostatic force
  - b. Vanderwall force
  - c. Gravitational force
  - d. Potential force.
8. Which of the following are semiconductors? [ a ]
  - a. Si and Ge
  - b. Li and Na
  - c. Fe and Co
  - d. O<sub>2</sub> and N<sub>2</sub>.

***Fill in the blanks:***

1. Molecular orbital is -----centric?
2. The shape of the *d-orbital* is -----.
3. According to the molecular orbital theory magnetic nature of the Oxygen is -----.
4. Energy gap between valence band and conduction band maximum in -----.
5. Atomic orbital is -----centric?
6. The shape of the *p-orbital* is -----.
7. According to the molecular orbital theory magnetic nature of the *Nitrogen* is -----.
8. Energy gap between Valence band and Conduction band is minimum in -----.

## **WATER AND ITS TREATMENT**

## **INTRODUCTION:**

Water is nature's most wonderful, abundant and useful compound. Water is not only essential for the lives of animals and plants, but also occupies a unique position in industries. It is widely used in drinking, bathing, sanitary, washing, irrigation, fire-fights, air-conditioning and also production of industrial materials. The distribution of water on the Earth's surface is extremely uneven. Only 3% Of freshwater (69% resides in glaciers, 30% underground, and less than 1% is located in lakes, rivers and swamps.) of water on the surface is fresh; the remaining 97% resides in the ocean. Looked at another way, only one percent of the water on the Earth's surface is usable by humans, and 99% of the usable quantity is situated underground.

### **Types of Impurities present in water:**

The natural water is usually contaminated by different types of impurities.

They are mainly three types. **i.** Physical impurities **ii.** Chemical impurities **iii.** Biological impurities

### **1. Physical impurities:**

- *Colour:* in water is caused by metallic substances like salts.
  - *Turbidity:* is due to the colloidal, extremely fine suspensions such as insoluble substances like clay, slit, and micro-organisms.
  - *Taste:* presence of dissolved minerals in water produces taste. Bitter taste can be due to the presence of Fe, Al, Mn, Sulphates and lime. Soap taste can be due to the presence of large amount of sodium bicarbonate.
  - *Odour:* In water is undesirable for domestic as well as industrial purpose.

## 2. Chemical impurities:

- *Inorganic chemicals:* Cations( $\text{Al}^{+3}$ ,  $\text{Ca}^{+2}$ ,  $\text{Mg}^{+2}$ ,  $\text{Fe}^{+2}$ ,  $\text{Zn}^{+2}$ ,  $\text{Cu}^{+2}$   $\text{Na}^+$ ,  $\text{K}^+$ ), Anions( $\text{Cl}^-$ ,  $\text{SO}_4^{-2}$ ,  $\text{NO}_3^-$ ,  $\text{HCO}_3^-$ ,  $\text{F}^-$ ,  $\text{NO}_2^-$ )
  - *Organic chemicals:* dyes, paints, petroleum products, pesticides, detergents, drugs textile materials, other organic related materials.

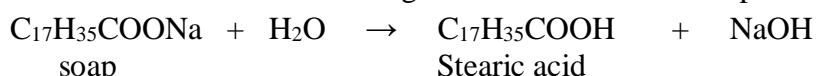
### **3. Biological Impurities:**

- Biological impurities are Algae, pathogenic bacteria, fungi, viruses, pathogens, parasite-worms.

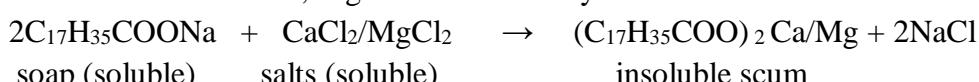
## HARDNESS OF WATER

**Hardness of water** defined as which prevent the lathering of soap. This is due to presence of certain salts like  $\text{Ca}^{+2}$ ,  $\text{Mg}^{+2}$  and other heavy metals dissolved in water. Soaps (Sodium or Potassium salts of higher fatty acids) like Stearic acids ( $\text{C}_{17}\text{H}_{35}\text{COONa}$ ).

**Soft Water:** The water which gives more lather with soap is called soft water.



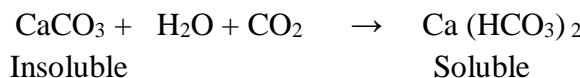
**Hard Water:** The water which does not give lather with soap is called hard water. This is due to presence of certain salts like  $\text{Ca}^{+2}$ ,  $\text{Mg}^{+2}$  and other heavy metals dissolved in water



**CAUSES OF HARDNESS**

Hardness of water is due to the presence of Bicarbonates, Chlorides, Sulphates and Nitrates of Calcium and Magnesium. These soluble salts get mixed with natural water due to the following reasons:

- When natural water containing  $\text{CO}_2$  flows over the rocks of the limestone ( $\text{CaCO}_3$ ) and Dolomite ( $\text{CaCO}_3 \& \text{MgCO}_3$ ), they get converted into soluble bicarbonates. Thus, water gets hardness.



- When natural water flows over the rocks containing chlorides and sulphates and Nitrates of Calcium and magnesium, these salts dissolve in water. Thus water gets hardness.

**DISADVANTAGES OF HARDNESS****1. In Domestic use:**

- **Washing:** Hard water, when used for washing purposes, does not produce lather freely with soap. As a result cleaning quality of soap is decreased and a lot of it is wasted.
- **Bathing:** Hard water does not lather freely with soap solution, but produces sticky scum on the bathtub and body. Thus, the cleaning quality of soap is depressed and a lot of it is wasted.
- **Cooking:** The boiling point of water is increased because of presence of salts. Hence more fuel and time are required for cooking.
- **Drinking:** Hard water causes bad effects on our digestive system. Moreover, the possibility of forming calcium oxalate crystals in urinary tracks is increased.

**2. Industrial Use:**

- **Textile Industry:** Hard water causes wastage of soap. Precipitates of calcium and magnesium soaps adhere to the fabrics and cause problem.
- **Sugar Industry:** The water which contains sulphates, nitrates, alkali carbonates are used in sugar refining, cause difficulties in the crystallization of sugar.
- **Dyeing Industry:** The dissolved salts in hard water may react with costly dyes forming precipitates.
- **Paper Industry:** Calcium, magnesium, Iron salts in water may affect the quality of paper.
- **Pharmaceutical Industry:** Hard water may cause some undesirable products while preparation of pharmaceutical products.

**3. Steam generation in Boilers:**

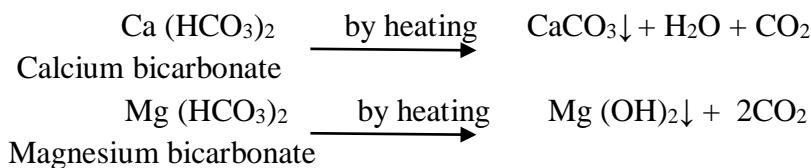
- For steam generation, boilers are almost invariably employed. If the hard water is fed directly to the boilers, there arise many troubles such as: Scales & sludges formation, Corrosion, Priming & Foaming and Caustic embrittlement.

**TYPES OF HARDNESS**

**Hardness of water is mainly two types:**

1. Temporary Hardness
2. Permanent Hardness

**1. Temporary Hardness:** Temporary Hardness mainly caused by the presence of dissolved bicarbonates of Calcium, Magnesium ( $\text{Ca}(\text{HCO}_3)_2$ ,  $\text{Mg}(\text{HCO}_3)_2$ ). Temporary Hardness can be largely removed by boiling of water.



**2. Permanent Hardness:** It is due to the presence of dissolved Chlorides, Nitrates and Sulphates of Calcium, Magnesium, Iron and other metals. Permanent hardness responsible salts are  $\text{CaCl}_2$ ,  $\text{MgCl}_2$ ,  $\text{CaSO}_4$ ,  $\text{MgSO}_4$ ,  $\text{FeSO}_4$ ,  $\text{Al}_2(\text{SO}_4)_3$ . Permanent Hardness cannot be removed by boiling but it can be removed by the use of *chemical agents*.

**EXPRESSION OF HARDNESS**

The expression of hardness producing salts usually expressed in terms of an equivalent amount of  $\text{CaCO}_3$ . Calcium Carbonate is chosen as a standard because:

- i. Its molecular weight (100) and equivalent weight (50) is a whole number, so the calculations in water analysis can be simplified.
- ii. It is the most insoluble salt that can be precipitated in water treatment.

The conversion of the hardness causing salts into  $\text{CaCO}_3$  equivalents can be achieved by using the following formula:

$$\text{Degree of Hardness} = \frac{\text{The weight of hardness causing salts}}{\text{Molecular weight of hardness causing salts}} \times 100 \text{ (Molecular weight of CaCO}_3)$$

**UNITS OF HARDNESS**

**1. Parts per Million (ppm):** The number of parts of calcium carbonate equivalent hardness presents in  $10^6$  parts of water.

$$1 \text{ ppm} = 1 \text{ part of CaCO}_3 \text{ eq hardness in } 10^6 \text{ parts of water.}$$

**2. Milligrams per litre (mg/l):** The number of milligrams of calcium carbonate equivalent hardness presents in litre of water.

$$1 \text{ mg/L} = 1 \text{ mg of CaCO}_3 \text{ eq hardness in 1 litre of water.}$$

$$\text{But one litre of water weights } = 1 \text{ kg} = 1000 \text{ g} = 1000 \times 1000 \text{ mg} = 10^6 \text{ mg} = 1 \text{ ppm.}$$

**3. Clark's degree ( $^{\circ}\text{Cl}$ ):** The number of parts of calcium carbonate equivalent hardness presents in 70,000 or ( $7 \times 10^4$ ) parts of water.

$1^{\circ} \text{ Clarke} = 1 \text{ part of } \text{CaCO}_3 \text{ eq hardness per 70,000 parts of water.}$

**4. Degree French ( $^{\circ}\text{Fr}$ ):** The number of parts of calcium carbonate equivalent hardness presents in  $10^5$  parts of water.

$1^{\circ} \text{ Fr} = 1 \text{ part of } \text{CaCO}_3 \text{ hardness eq per } 10^5 \text{ parts of water.}$

**Relationship between various units of hardness:**

1 ppm	= 1 mg/L	= 0.1° Fr	= 0.07° Cl
1 mg/L	= 1 ppm	= 0.1° Fr	= 0.07° Cl
1 ° Cl	= 1.433° Fr	= 14.3 ppm	= 14.3 mg/L
1 ° Fr	= 10 ppm	= 10 mg/L	= 0.7° Cl

**Problem-1:** A sample of water is found to contains following dissolving salts in milligrams per litre  $\text{Mg}(\text{HCO}_3)_2 = 73$ ,  $\text{CaCl}_2 = 111$ ,  $\text{Ca}(\text{HCO}_3)_2 = 81$ ,  $\text{MgSO}_4 = 40$  and  $\text{MgCl}_2 = 95$ . Calculate temporary and permanent hardness and total hardness.

**Solution:**

Name of the hardness causing salts	Amount of the hardness causing salts(mg/Lit)	Molecular weight of hardness causing salts	Amounts equivalent to $\text{CaCO}_3$ (mg/Lit)
$\text{Mg}(\text{HCO}_3)_2$	73	146	$73 \times 100 / 146 = 50$
$\text{CaCl}_2$	111	111	$111 \times 100 / 111 = 100$
$\text{Ca}(\text{HCO}_3)_2$	81	162	$81 \times 100 / 162 = 50$
$\text{MgSO}_4$	40	120	$40 \times 100 / 120 = 33.3$
$\text{MgCl}_2$	95	95	$95 \times 100 / 95 = 100$

$$\begin{aligned} \text{Temporary hardness} &= \text{Mg}(\text{HCO}_3)_2 + \text{Ca}(\text{HCO}_3)_2 \\ &= 50 + 50 = 100 \text{ mgs/Lit.} \end{aligned}$$

$$\begin{aligned} \text{Permanent hardness} &= \text{CaCl}_2 + \text{MgSO}_4 + \text{MgCl}_2 \\ &= 100 + 33.3 + 100 = 233.3 \text{ mgs/Lit.} \end{aligned}$$

$$\begin{aligned} \text{Total hardness} &= \text{Temporary hardness} + \text{Permanent hardness} \\ &= 100 + 233.3 = 333.3 \text{ mgs/Lit.} \end{aligned}$$

**Problem-2:** A sample of water is found to contains following dissolving salts in milligrams per litre  $\text{Mg}(\text{HCO}_3)_2 = 16.8$ ,  $\text{MgCl}_2 = 12.0$ ,  $\text{MgSO}_4 = 29.6$  and  $\text{NaCl} = 5.0$ . Calculate temporary and permanent hardness of water.

**Solution:**

Name of the hardness causing salts	Amount of the hardness causing salts(mg/Lit)	Molecular weight of hardness causing salts	Amounts equivalent to $\text{CaCO}_3$ (mg/Lit)
$\text{Mg}(\text{HCO}_3)_2$	16.8	146	$16.8 \times 100 / 146 = 11.50$
$\text{MgCl}_2$	12.0	95	$12.0 \times 100 / 95 = 12.63$
$\text{MgSO}_4$	29.6	120	$29.6 \times 100 / 120 = 24.66$
$\text{NaCl}$	5.0	NaCl does not contribute any hardness to water hence it is ignored.	

## UNIT-II

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$$\begin{aligned}\text{Temporary hardness} &= \text{Mg}(\text{HCO}_3)_2 \\ &= 11.50 \text{mgs/Lit.}\end{aligned}$$

$$\begin{aligned}\text{Permanent hardness} &= \text{MgCl}_2 + \text{MgSO}_4 \\ &= 12.63 + 24.66 = 37.29 \text{mgs/Lit.}\end{aligned}$$

**Problem-3:** A sample of water is found to contains following analytical data in milligrams per litre  $\text{Mg}(\text{HCO}_3)_2 = 14.6$ ,  $\text{MgCl}_2 = 9.5$ ,  $\text{MgSO}_4 = 6.0$  and  $\text{Ca}(\text{HCO}_3)_2 = 16.2$ . Calculate temporary and permanent hardness of water in parts per million, Degree Clarke's and Degree French.

**Solution:**

Name of the hardness causing salts	Amount of the hardness causing salts(mg/Lit)	Molecular weight of hardness causing salts	Amounts equivalent to $\text{CaCO}_3$ (mg/Lit)
$\text{Mg}(\text{HCO}_3)_2$	14.6	146	$14.6 \times 100 / 146 = 10$
$\text{MgCl}_2$	9.5	95	$9.5 \times 100 / 95 = 10$
$\text{MgSO}_4$	6.0	120	$6.0 \times 100 / 120 = 5$
$\text{Ca}(\text{HCO}_3)_2$	16.2	162	$16.2 \times 100 / 162 = 10$

$$\begin{aligned}\text{Temporary hardness } [\text{Mg}(\text{HCO}_3)_2 + \text{Ca}(\text{HCO}_3)_2] &= 10 + 10 = 20 \text{mg/Lit} \\ &= 20 \text{ppm} \\ &= 20 \times 0.07^\circ\text{Cl} = 1.4^\circ\text{Cl} \\ &= 20 \times 0.1^\circ\text{Fr} = 2^\circ\text{Fr}\end{aligned}$$

$$\begin{aligned}\text{Permanent hardness } [\text{MgCl}_2 + \text{MgSO}_4] &= 10 + 5 = 15 \text{mg/Lit} \\ &= 15 \text{ppm} \\ &= 15 \times 0.07^\circ\text{Cl} = 1.05^\circ\text{Cl} \\ &= 15 \times 0.1^\circ\text{Fr} = 1.5^\circ\text{Fr}\end{aligned}$$

**Problem-4:** Calculate the amount of temporary and permanent hardness of a water sample in Degree Clarke's, Degree French and Milligrams per Litre which contains following impurities.

$$\text{Ca}(\text{HCO}_3)_2 = 121.5 \text{ ppm}, \text{Mg}(\text{HCO}_3)_2 = 116.8 \text{ ppm}, \text{MgCl}_2 = 79.6 \text{ ppm} \text{ and } \text{CaSO}_4 = 102 \text{ ppm.}$$

**Solution:**

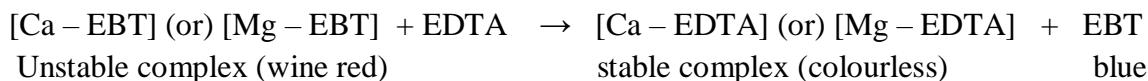
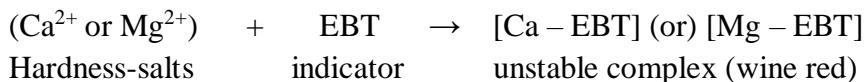
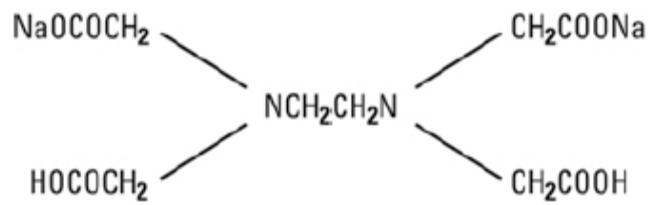
Name of the hardness causing salts	Amount of the hardness causing salts(ppm)	Molecular weight of hardness causing salts	Amounts equivalent to $\text{CaCO}_3$ (ppm)
$\text{Ca}(\text{HCO}_3)_2$	121.5	162	$121.5 \times 100 / 162 = 75$
$\text{Mg}(\text{HCO}_3)_2$	116.8	146	$116.8 \times 100 / 146 = 80$
$\text{MgCl}_2$	79.6	95	$79.6 \times 100 / 95 = 3.37$
$\text{CaSO}_4$	102	136	$102 \times 100 / 136 = 75$

$$\begin{aligned}\text{Temporary hardness } [\text{Mg}(\text{HCO}_3)_2 + \text{Ca}(\text{HCO}_3)_2] &= 75 + 80 = 155 \text{ ppm} \\ &= 155 \times 0.07^\circ\text{Cl} = 10.85^\circ\text{Cl} \\ &= 155 \times 0.1^\circ\text{Fr} = 15.5^\circ\text{Fr} \\ &= 155 \times 1 \text{mg/Lit} = 155 \text{ mg/Lit}\end{aligned}$$

$$\begin{aligned}\text{Permanent hardness } [\text{MgCl}_2 + \text{CaSO}_4] &= 10 + 5 = 15 \text{mg/Lit} \\ &= 15 \text{ppm} \\ &= 15 \times 0.07^\circ\text{Cl} = 1.05^\circ\text{Cl} \\ &= 15 \times 0.1^\circ\text{Fr} = 1.5^\circ\text{Fr}\end{aligned}$$

### DETERMINATION OF HARDNESS BY COMPLEXOMETRIC METHOD / EDTA METHOD

**Principle:** The determination of hardness is carried out by titrating water sample with Sodium salt of Ethylene Diamine Tetra Acetic Acid (EDTA) using Eriochrome Black-T as an indicator and keeping the pH of the water at 9.0 - 10.0. The end point is the change in colour from wine - red to blue, when the EDTA solution complexes the calcium and magnesium salt completely.



**Chemicals Required:**

- i. Preparation of standard hard water (0.01M): Dissolve 1g of pure, dry  $\text{CaCO}_3$  in 1 Litre solution.
- ii. Preparation of EDTA solution: Dissolve 4 g of pure EDTA crystals in 1 Litre of distilled water.
- iii. Preparation of Indicator (EBT): Dissolve 0.5 g of Eriochrome Black-T in 100mL alcohol.
- iv. Preparation of Buffer solution: Add 67.5g of  $\text{NH}_4\text{Cl}$  to 570 ml of Con. Ammonia solution and then dilute with distilled water to 1 Litre.

**Various steps involved in this method:**

1. **Standardization of EDTA solution:** Rinse and fill the burette with EDTA solution. Pipette out 20 ml of standard hard water ( $M_1$ ) in a conical flask. Add 4ml of buffer solution and 2 drops of EBT indicator. Titrate with EDTA solution till wine-red colour changes to clear blue. Let volume used by 'X' ml.

$$M_1 V_1 = M_2 V_2$$

Where,  $M_1$  = Molarity of Standard Hard water (0.01M),

$V_1$  = Volume of Standard Hard water (20 ml),

$M_2$  = Molarity of EDTA,

$V_2$  = Volume of EDTA (Xml).

2. **Determination of Total Hardness:** Rinse and fill the burette with EDTA solution. Pipette out 20 ml of sample water ( $V_3$ ) in a conical flask. Add 4 ml of buffer solution and 2 drops indicator. Titrate with EDTA solution till wine-red colour changes to clear blue. Let volume used by 'Y' ml.

$$M_2 V_2 = M_3 V_3$$

Where,  $M_2$  = Molarity of EDTA,  
 $V_2$  = Volume of EDTA (Yml).  
 $M_3$  = Molarity of sample water,  
 $V_3$  = Volume of Sample water (20 ml).

$$\begin{aligned}\text{Total Hardness} &= M_3 \times \text{Molecular weight of CaCO}_3 (100) \times \text{One Litre (1000ml)} \\ &= M_3 \times 10^5 \text{ ppm}\end{aligned}$$

**3. Determination of Permanent Hardness:** Take 100 ml of sample water in 250 ml beaker. Boil it to remove temporary hardness to about half of its volume and cool to room temperature, filter through filter paper to remove insoluble salts. Make up the volume to the original 100ml by adding distilled water. Now Pipette out 20 ml of this solution ( $V_4$ ) in a conical flask. Add 4 ml of buffer solution and 2 drops indicator. Titrate with EDTA solution till wine-red colour changes to clear blue. Let volume used by 'Z' ml.

$$M_2 V_2 = M_4 V_4$$

Where,  $M_2$  = Molarity of EDTA,  
 $V_2$  = Volume of EDTA (Z ml).  
 $M_4$  = Molarity of Permanent hard water,  
 $V_4$  = Volume of Permanent hard water (20 ml)

$$\begin{aligned}\text{Permanent Hardness} &= M_4 \times \text{Molecular weight of CaCO}_3 (100) \times \text{One Litre (1000ml)} \\ &= M_4 \times 10^5 \text{ ppm}\end{aligned}$$

**4. Determination of Temporary Hardness:**

$$\text{Temporary Hardness} = \text{Total Hardness} - \text{Permanent Hardness}$$

**Problem-1:** 50 ml of standard hard water containing 1 gram of pure  $\text{CaCO}_3$  per liter consumed 20 ml of EDTA. 50 ml of hard water consumed 25 ml of same EDTA solution EBT indicator. Calculate the total hardness of water sample in ppm.

**Solution:**

**Strength of standard hard water sample ( $\text{CaCO}_3$  solution)  $M_1$ =**

$$\begin{aligned}&\frac{\text{Weight of CaCO}_3}{\text{Mol. wt of CaCO}_3} \times \frac{1000}{1000} \\ &= \frac{1 \text{ gm}}{100} \times \frac{1000}{1000} = 0.01 \text{ M}\end{aligned}$$

$$\text{Strength of EDTA solution } M_2 = \frac{V_1 M_1}{V_2} = \frac{50 \times 0.01}{20} = 0.025 \text{ M}$$

$V_1$  = Volume of standard hard water (50 ml),  $M_1$  = Strength of standard hard water (0.01M)

$V_2$  = Volume of EDTA solution (20 ml),  $M_2$  = Strength of EDTA solution =?

$$\text{Calculation of Total hardness } M_3 = \frac{V_2 M_2}{V_3} = \frac{25 \times 0.025}{50} = 0.0125 \text{ M}$$

$V_2$  = Volume of EDTA solution (25 ml),  $M_2$  = Strength of EDTA solution = 0.025M  
 $V_3$  = Volume of sample hard water (50 ml),  $M_3$  = Strength of sample hard water =?

$$\begin{aligned}\text{Total Hardness} &= 0.0125 \times 10^5 \text{ ppm} \\ &= 0.0125 \times 100 (\text{Mol. Wt of CaCO}_3) \times 1000 (\text{ml}) \text{ppm} \\ &= 1250 \text{ ppm.}\end{aligned}$$

## UNIT-II

**Problem-2:** 0.28 grams of  $\text{CaCO}_3$  were dissolved in HCl and the solution was made upto one litre with distilled water. 100 ml of the above solution required 28 ml of EDTA solution on titration. 100 ml of hard water sample consumed 33 ml of same EDTA solution EBT indicator. 100 ml of this water after boiling cooling and filtering required 10 ml of EDTA solution in titration. Calculate the permanent and temporary hardness of water sample in ppm.

$$\text{Strength of standard hard water sample (CaCO}_3 \text{ solution) } M = \frac{\text{Weight of CaCO}_3}{\text{Mol. wt of CaCO}_3} \times \frac{1000}{1000}$$

$$= \frac{0.28 \text{ gm}}{100} \times \frac{1000}{1000} = 0.0028 \text{ M}$$

$$\text{Strength of EDTA solution } M_2 = \frac{V_1 M_1}{V_2} = \frac{100 \times 0.0028}{28} = 0.01 \text{ M}$$

$V_1$  = Volume of standard hard water (100 ml),  $M_1$  = Strength of standard hard water (0.0028M)

$V_2$  = Volume of EDTA solution (28 ml),  $M_2$  = Strength of EDTA solution=?

$$\text{Calculation of Total hardness } M_3 = \frac{V_2 M_2}{V_3} = \frac{33 \times 0.01}{100} = 0.0033 \text{ M}$$

$V_2$  = Volume of EDTA solution (33 ml),  $M_2$  = Strength of EDTA solution (0.01M)  
 $V_3$  = Volume of sample hard water (100 ml),  $M_3$  = Strength of sample hard water=?

$$\text{Total Hardness} = 0.0033 \times 10^5 \text{ ppm} = 0.0033 \times 100 (\text{Mol. Wt of CaCO}_3) \times 1000 (\text{ml})\text{ppm} \\ = 330 \text{ ppm}$$

$$\text{Calculation of Permanent hardness } M_4 = \frac{V_2 M_2}{V_4} = \frac{10 \times 0.01}{100} = 0.001 \text{ M}$$

$V_2$  = Volume of EDTA solution (10 ml),  $M_2$  = Strength of EDTA solution (0.01M)

$V_4$  = Volume of sample hard water after boiling cooling and filtering (100 ml)

$M_4$  = Strength of sample hard water after boiling cooling and filtering=?

$$\text{Permanent Hardness} = 0.001 \times 10^5 \text{ ppm} \\ = 0.001 \times 100 (\text{Mol. Wt of CaCO}_3) \times 1000 (\text{ml})\text{ppm} \\ = 100 \text{ ppm}$$

$$\text{Calculation of Temporary hardness} = \text{Total hardness} - \text{Permanent hardness} \\ = 330 - 100 = 230 \text{ ppm}$$

### **POTABLE WATER AND ITS SPECIFICATIONS**

Water free from contaminants or water that is safe for human consumption is called potable water. The following are the **specifications of water drinking purpose**.

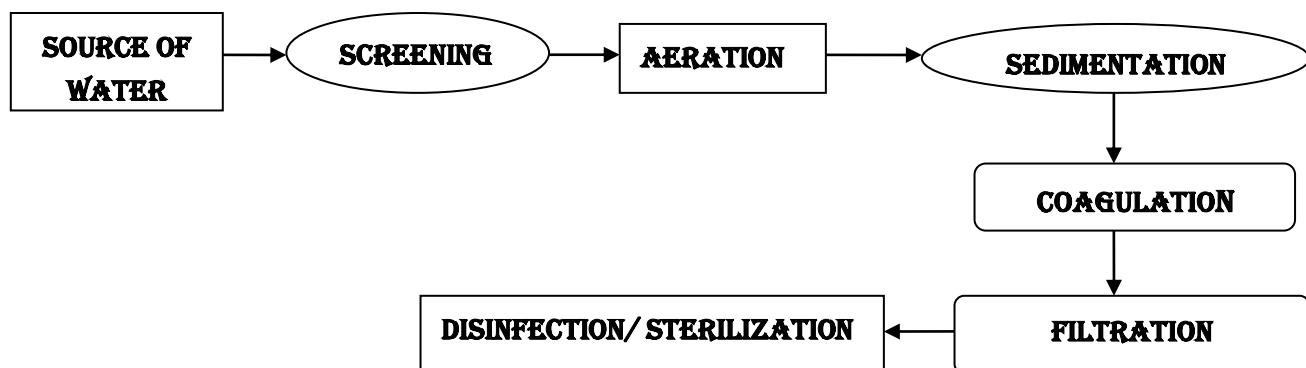
1. The water should be clear (colorless), odorless and pleasant taste.
2. The optimum *hardness* of water must be 125ppm.
3. The *pH* of potable water should be 7.0 to 8.5.
4. The recommended maximum concentration of *total dissolved solids (TDS)* in potable water must not exceed 500 ppm.
5. The *turbidity* in drinking water should not exceed 25 ppm.

6. The water must be free from *heavy metals* like Lead, Arsenic, Chromium and Manganese.
7. The water must be *free from pathogenic bacteria*
8. The water must be *free from dissolved gases* like H<sub>2</sub>S, CO<sub>2</sub> and NH<sub>3</sub>.

### STEPS INVOLVED IN THE TREATMENT OF POTABLE WATER

Treatment of water for drinking purposes mainly includes the removal of suspended impurities, colloidal impurities and harmful pathogenic bacteria. The following stages are involved in purification.

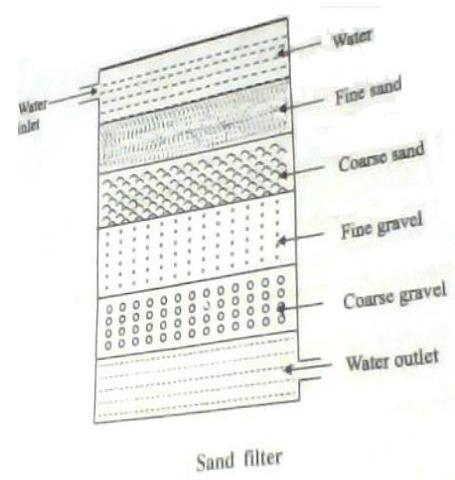
- 1. Screening:** The water is passed through screens having larger number of holes; it retains floating impurities like wood pieces, leaves, heavier objectives etc.,
- 2. Aeration:** The water is then subjected to aeration (reacting with air) which helps in exchange of gases between water and air, increases the oxygen content and removes the impurities like iron, manganese and dissolved gases like H<sub>2</sub>S, CO<sub>2</sub> and NH<sub>3</sub>.



- 3. Sedimentation:** In this process water is allowed to stand for 2-6 hours without any disturbance, 75 % of suspended and colloidal impurities are settled down under gravitational force.

- 4. Coagulation:** Coagulants like alum, sodium aluminates and Aluminum sulphate are added which produce gelatinous precipitates called flock. Flock attracts and helps accumulation of the colloidal particles resulting in setting of the colloidal particles.

- 5. Filtration:** Filtration helps in removal of the colloidal and suspended impurities not removed by sedimentation. Usually sand filters are employed. In this filtration fine sand layer on the top supported by coarse sand layer, which is supported by gravel.



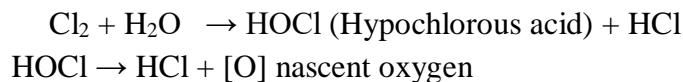
- 6.** The colloidal impurities are retained by the fine sand layer resulting in the very slow filtration of water. Periodically the top layers of the fine sand layer is scraped off, washed, dried and introduced into the filter bed for reuse.

- 7. Disinfection of water by sterilization:** The process of destroying the harmful bacteria's is known as sterilization or disinfection.

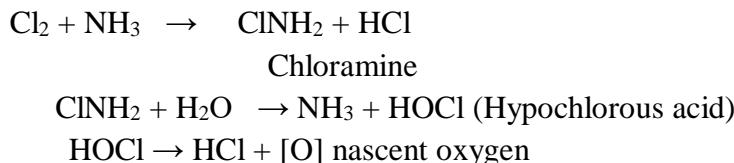
**DISINFECTION INCLUDES THE FOLLOWING METHODS OF POTABLE WATER**

**1. By Chlorination:** The process of adding chlorine to water is called chlorination. Chlorination can be done by the following methods.

**a. By adding Chlorine gas:** Chlorine gas is a very good disinfectant, which can be bubbled in the water. In this process calculated amount of chlorine gas is passed in order to destroy the pathogenic bacteria is called chlorination. Chlorine is also reacts with water and generates hypochlorous acid and nascent oxygen, which acts a powerful oxidizing agent and kills the bacteria.

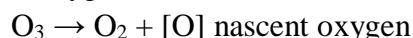


**b. By adding Chloramine:** When chlorine and ammonia are mixed in the ratio 2:1 a compound chloramine is formed.



Chloramine compounds decompose slowly to give nascent oxygen which will be act as good disinfectant than the Chlorine. Chloramine gives good taste to the treated water.

**2. By Ozonization:** Ozone is a powerful disinfectant and is readily absorbed by water. Ozone is highly unstable and breaks down to give nascent oxygen.



The nascent oxygen is a powerful oxidizing agent and kills the bacteria.

**Disadvantages:** This process is costly and cannot be used in large scale, due to unstable of ozone cannot be stored for long time.

**BOILER TROUBLES**

A boiler is a closed vessel in which water under pressure is transformed into steam by the application of heat. The steam so generated is used in industries and generation of power. In modern pressure boilers and laboratories, the water required is used pure than the distilled water.

A boiler feed water should correspond with the following composition:

- Its hardness should be below 0.2ppm.
- Its caustic alkalinity (due to  $\text{OH}^-$ ) should lie between 0.15ppm to 0.45ppm.
- It's should be free from dissolved gases like  $\text{O}_2$ ,  $\text{CO}_2$ , in order to prevent boiler corrosion.

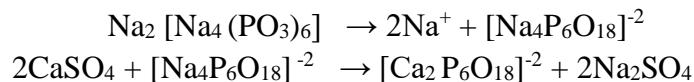
**INTERNAL TREATMENT OF WATER**

Suitable chemicals are added to the boiler water either to precipitate or to convert the scale into compounds is called **internal treatment** of the boiler feed water. Internal treatment can be done following types.

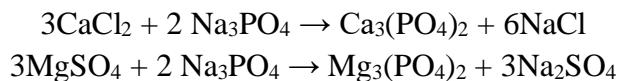
## UNIT-II

**1. Calgon conditioning:** Involves in adding calgon to boiler water. It prevents the scale and sludge formation by forming soluble complex compound with  $\text{CaSO}_4$ .

Calgon = Sodium hexa meta phosphate =  $\text{Na}_2[\text{Na}_4(\text{PO}_3)_6]$



**2. Phosphate conditioning:** The addition of sodium phosphate in hard water reacts with the hardness causing agents and gives calcium and magnesium phosphates which are soft and non-adhere and can be removed easily by blow-down operation.



Generally three types of Phosphates are employed.

- Tri sodium Phosphate ( $\text{Na}_3\text{PO}_4$ ): is too alkaline used for treat to too acidic water.
- Di sodium Phosphate ( $\text{Na}_2\text{HPO}_4$ ): is weakly alkaline used for treat to weakly acidic water.
- Sodium dihydrogen Phosphate ( $\text{NaH}_2\text{PO}_4$ ): is too acidic used for treat to too alkaline water.

**3. Colloidal conditioning:** The addition of organic substances such as Kerosene, tannin, Gel. These substances gets coated over the scale forming precipitates and gives a loose and non-sticky precipitates which can be removed by using blow-down operation.

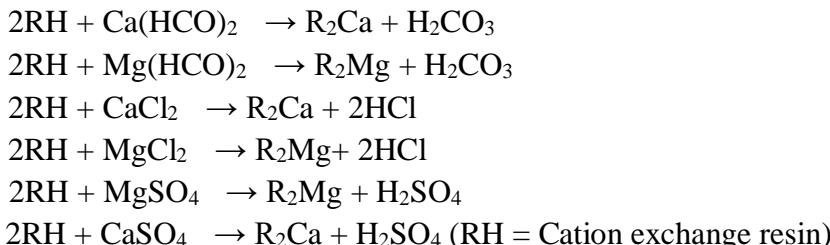
### **EXTERNAL TREATMENT OF WATER - ION EXCHANGE PROCESS**

Ion exchange process is also known as demineralization process. Ion- Exchange resins are insoluble. Cross linked long chain organic polymers with a micro porous structure, and the “functional Groups” attached to the chains are responsible for the ion-exchanging properties. Resins with acidic functional group are capable of exchanging  $\text{H}^+$  ions with other cations. Resins with basic functional groups are capable of exchanging  $\text{OH}^-$  ions with other anions.

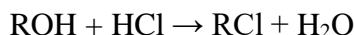
Resins are classified as:

- Cation Exchange Resins
- Anion Exchange Resins.

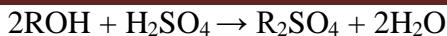
**i. Cation Exchange Resins:** Cation exchange resins are styrene divinyl benzene co-polymers, which on sulphonation (or) carboxylation, which contains  $-\text{COOH}$ ,  $-\text{SO}_3\text{H}$  functional groups which responsible for exchanging their hydrogen ions with cations in water.



**ii. Anion Exchange Resins:** Anion exchange resins are Phenol formaldehyde (or) amine formaldehyde copolymers, which contains amino or basic functional groups which responsible for exchanging their  $\text{OH}^-$  ions with anions in water.



## UNIT-II



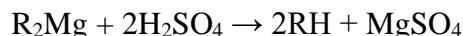
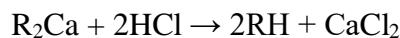
In ion-exchange process, hard water is allowed to pass through cation exchange resins, which remove  $\text{Ca}^{+2}$  and  $\text{Mg}^{+2}$  ions and exchange equivalent amount of  $\text{H}^+$  ions. Anions exchange resins remove bicarbonates, chlorides and sulphates from water exchange equivalent amount of  $\text{OH}^-$  ions.

Thus by passing hard water through cation hardness is observed by the following reactions.  $\text{H}^+$  and  $\text{OH}^-$  ions, thus released in water from respective cation and anion exchange columns, get combined to produce water molecules.

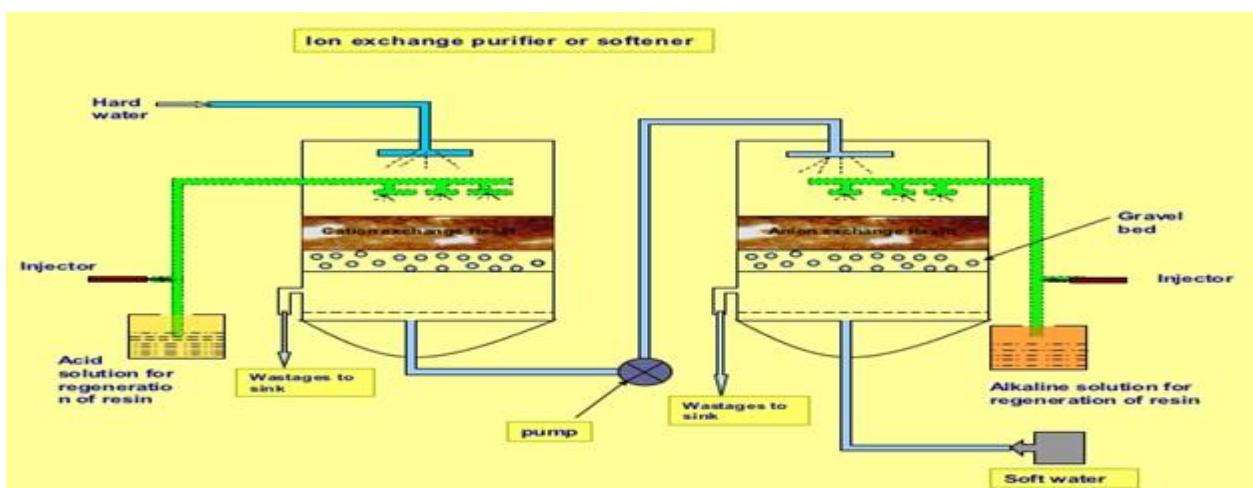
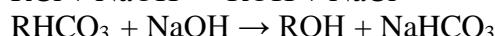
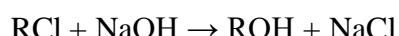
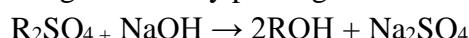


The water coming out from the exchanger is ion free from anions and cations. Thus water of zero hardness is obtained.

**Regeneration:** When cation exchanger losses capacity of producing  $\text{H}^+$  ions and exchanger losses capacity of producing  $\text{OH}^-$  ions, they are said to be exhausted. The exhausted cation exchanger is regenerated by passing it through dilute sulphuric acid.



The exhausted anion exchanger is regenerated by passing a dilute solution of  $\text{NaOH}$ .



### Merits of Ion-exchange process:

- The process can be used to soften highly acidic or alkaline water.
- It produces water of very low hardness (2ppm)
- So it is very good for treating water for use in high-pressure boilers.

### Demerits of Ion-exchange process:

- The equipment is costly and more expensive chemicals are needed.
- If water contains turbidity, the output of the process is reduced. The turbidity must be below 10ppm; else it has to be removed by coagulation and filtration.

## DESALINATION OF WATER (REVERSE OSMOSIS)

The process of removing common salt (Sodium Chloride) from the water is known as **desalination**.

The water containing dissolved salts with a salty or brackish taste is called **brackish water**.

Depending upon the quantity of dissolved solids, water is graded as:

- i. Fresh Water: Contains less than 1000 ppm of dissolved solids.
- ii. Brackish Water: Contains more than 1000 ppm to less than 35000 ppm of dissolved solids.
- iii. Sea Water: Contains more than 35000 ppm of dissolved solids.

Sea water and brackish water can be made available as drinking water through desalination process.

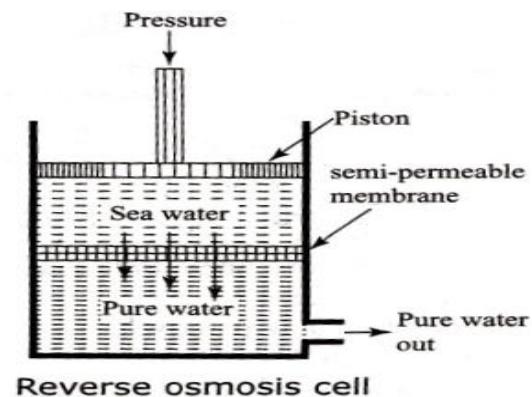
Desalination is carried out either by reverse osmosis or electro dialysis.

### **Reverse Osmosis:**

Reverse Osmosis is a process in which pressure greater than the osmotic pressure is applied on the high concentration side of the membrane, the flow of solvent move from concentrated side to dilute side across the membrane.

Osmosis is the phenomenon by virtue of which flow of solvent takes place from a region of low concentration to high concentration when two solutions of different concentrations are separated by a semi-permeable membrane.

In this process pure water is separated from salt water. 15-40 kg/cm<sup>2</sup> pressure is applied for separating the water from its contaminants. The membranes used are cellulose acetate, polymethyl acrylate and polyamide polymers. The process is also known as **super or hyper filtration**.



### **Advantages:**

- It is simple and reliable process & Capital and operating expenses are low.
- The life of the semi-permeable membrane is about two years and it can be easily replaced within a few minutes, thereby nearly uninterrupted water supply can be provided.

## BOILER TROUBLES

A boiler is a closed vessel in which water under pressure is transformed into steam by the application of heat. The steam so generated is used in industries and generation of power. In treatment of water complete elimination of all the impurities is not possible. The impurity that gives rise to certain troubles will be removed to certain extent. In modern pressure boilers and laboratories, the water required is used pure than the distilled water.

A boiler feed water should correspond with the following composition:

- Its hardness should be below 0.2ppm.
- Its caustic alkalinity (due to OH<sup>-</sup>) should lie between 0.15ppm to 0.45ppm.
- It's should be free from dissolved gases like O<sub>2</sub>, CO<sub>2</sub>, in order to prevent boiler corrosion.

Excess of impurities in the boiler feed water generally cause the following problems:

1. Sludge's and Scale formation
2. Caustic embrittlement

**1. Sludge's and Scale formation:** Boilers are employed for the steam generation in power plants, where water is continuously heated to produce steam. As more and more water is removed from water in the form of steam, the boiler water gets concentrated with dissolved salts progressively reaches the saturation point. At this point the dissolved salts are precipitated out and slowly settle on the inner walls of the boiler plate. The precipitation takes place in two ways.

**Sludge** is a soft, loose and slimy precipitate formed within the boiler. It is formed at comparatively colder portions of the boiler and collects in the area where flow rate is slow.

Ex:  $MgCO_3$ ,  $MgCl_2$ ,  $CaCl_2$ ,  $MgSO_4$ .

**Reasons for formation of sludges:**

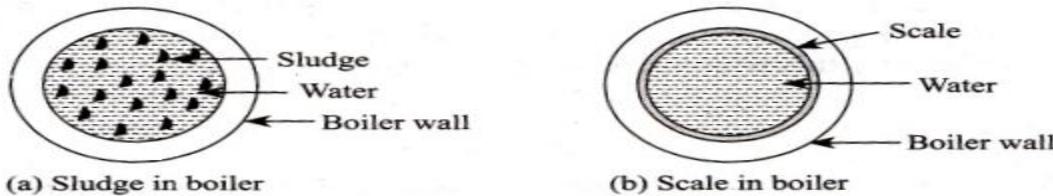
1. The dissolved salts whose solubility is more in hot water and less in cold water produce sludges.

**Disadvantages of sludges:**

2. Sludges are bad conductors of heat and results in the wastage of heat and fuel.
3. Excessive sludge formation leads to the settling of sludge in slow circulation areas such as pipe connections, plug openings, gauge-glass connections leading to the choking of the pipes.

**Prevention of sludge formation:**

- a. By using soft water which is free from dissolved salts like  $MgCO_3$ ,  $MgCl_2$ ,  $CaCl_2$  and  $MgSO_4$  can be prevent sludge formation.
- b. By blow down operation carried out frequently can prevent sludge formation.



**Sludges and scales in boiler**

**Scale:** Scales are hard, adhering precipitates formed on the inner walls of the boilers. They stick very firmly on to the inner wall surface and are difficult to remove with chisel and hammer. Scales are formed by decomposition of calcium bicarbonate in low pressure boilers

**Reasons for formation of scales:**

- a. **Decomposition of calcium bicarbonate:** The calcium bicarbonate at high temperature decomposes to calcium carbonate which is insoluble salt, forms scale in low pressure boilers.



- b. **Decomposition of calcium sulphate:** The solubility of  $CaSO_4$  in water decreases with the increase in temperature and forms precipitation on the surface of the boiler further which forms hard scale. This type of scales is formed in high-pressure boilers.

- c. **Hydrolysis of Magnesium salts:** Magnesium salts gets hydrolyzed at high temperature forming  $Mg(OH)_2$  precipitation which forms salt type scale.



**d. Presence of silica:**  $\text{SiO}_2$  present even in small quantities, deposits as Calcium silicates ( $\text{CaSiO}_3$ ) or Magnesium silicates ( $\text{MgSiO}_3$ ). The deposits form hard scale and are very difficult to remove.

#### Disadvantages of Scales:

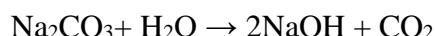
4. **Wastage of heat and fuels:** Scales poor thermal conductivity so that rate of heat transformation is reduced.
5. **Lowering of boiler safety** is due to overheating of the boiler material becomes softer and weaker, which causes distortion of boiler.
6. **Decrease in efficiency** of the boiler due to scales deposited in the valves and condensers of the boiler cause choking.
7. **Danger of explosion** which happens the formation of the scales, the boiler plate faces higher temperature outside and lesser temperature inside due to uneven expansion. The water comes suddenly in contact with overheated portion and larger amount steam is formed immediately, this results in development of sudden high pressure which may cause explosion of the boiler.

#### Removal of scales:

- c. If the scale formation is soft it can be removed by a scrapper, wire brush.
- d. By giving thermal shocks, by sudden heating and sudden cooling which makes scale brittle and removed by scrubbing with wire brush.
- e. If scale is very hard that is formed by  $\text{CaCO}_3$  can be removed by washing with 5-10% HCl and  $\text{CaSO}_4$  can be removed with EDTA solution.

## 2. Caustic Embrittlement:

The formation of brittle and in crystalline cracks in the boiler shell is called caustic embrittlement. The main reason for this is the presence of alkali-metal carbonates and bicarbonates in feed water and also the presence of sodium sulphate. In lime-soda process, it is likely that, some residual  $\text{Na}_2\text{CO}_3$  is still present in the softened water. This  $\text{Na}_2\text{CO}_3$  decomposes to give  $\text{NaOH}$  and  $\text{CO}_2$ , due to which the boiler water becomes "Caustic".



The  $\text{H}_2\text{O}$  evaporates, the concentration of  $\text{NaOH}$  increase progressively creating a concentration cell as given below thus dissolving the iron of the boiler as sodium ferrate ( $\text{Na}_2\text{FeO}_2$ ).

(-)Anode: 'Fe' at bents | Conc.NaOH || Dil.NaOH | 'Fe' at plane Surface: Cathode (+)

This causes embrittlement of boiler parts such as bends, joints, reverts etc, due to which the boiler gets fail. The iron at plane surfaces surrounded by dilute  $\text{NaOH}$  becomes cathodic while the iron at bends and joints surrounded by highly concentrated  $\text{NaOH}$  becomes anodic which consequently decayed or corroded.

#### Caustic embrittlement can be prevented:

- a. By maintaining the pH value of water and neutralization of alkali.
- b. By using Sodium Phosphate as softening reagents, in the external treatment of boilers.
- c. Caustic embrittlement can also be prevented by adding Tannin or Lignin or Sodium sulphate which prevents the infiltration of caustic-soda solution blocking the hair-cracks.

### ***Learning objectives:***

**After completion of this unit the student should be able to:**

- Introduction – hardness of water
- Causes of hardness.
- Types of hardness: temporary and permanent.
- Expression and units of hardness.
- Estimation of hardness of water by complexometric method.
- Potable water and its specifications.
- Steps involved in treatment of water – Disinfection of water by chlorination and ozonization.
- Boiler feed water and its treatment: Calgon conditioning
- Phosphate conditioning and Colloidal conditioning.
- External treatment of water – Ion exchange process.
- Desalination of water – Reverse osmosis.
- Numerical problems.

### ***Short Answer Questions:***

1. Distinguish between Temporary hardness and Permanent hardness.
2. Solve the following problem: A sample of water is found to contains following analytical data in milligrams per litre  $Mg(HCO_3)_2 = 14.6$ ,  $MgCl_2 = 9.5$ ,  $MgSO_4 = 6.0$  and  $Ca(HCO_3)_2 = 16.2$ . Calculate temporary and permanent hardness of water in parts per million, Degree Clarke's and Degree French.
3. Express the reasons why  $CaCO_3$  is selected expression of the hardness?
4. What is Calgon conditioning and Phosphate conditioning of boiler feed water.
5. What is the chemical name of Calgon.
6. What is break point chlorination?
7. Describe the conversion of 10 ppm of hardness of water in to degree clark.
8. Tell the advantages of ion exchange process?
9. Which chemicals are used for the regeneration of Cation and Anion exchange resins?

- 10.** State in your words about the specifications of Potable water.
- 11.** How to do the disinfection of potable water by chlorination and ozonization.
- 12.** How to calculate the amount of temporary and permanent hardness of a water sample in Degree Clarke's, Degree French and Milligrams per Litre which contains following impurities.  
 $\text{Ca}(\text{HCO}_3)_2 = 121.5 \text{ ppm}$ ,  $\text{Mg}(\text{HCO}_3)_2 = 116.8 \text{ ppm}$ ,  $\text{MgCl}_2 = 79.6 \text{ ppm}$  and  $\text{CaSO}_4 = 102 \text{ ppm}$ .

***Descriptive Questions:***

- 1.** How to estimate the hardness of water by using EDTA solution?
- 2.** Explain the Steps involved in the treatment of potable water.
- 3.** Explain steps involved in the treatment of potable water.
- 4.** Discuss softening of water using Ion exchange process.
- 5.** Define Desalination? Explain Reverse osmosis?
- 6.** Explain about Boiler feed water and its treatment.

***Objective Questions:***

- 1.** Which of the following will act as disinfectant? [ a ]  
**a.**  $\text{Cl}_2$                                    **b.**  $\text{O}_2$   
**c.**  $\text{F}_2$                                        **d.**  $\text{H}_2$
- 2.** EDTA method of determining hardness of water can be used to determine. [ a ]  
**a.** All types of hardness                           **b.** Temporary hardness only  
**c.** Permanent hardness only                      **d.** alkaline hardness only
- 3.** Coagulants help in the settling of. [ a ]  
**a.** Suspended impurities only                   **b.** Fine suspended matter only  
**c.** Colloidal particles only                       **d.** both (b) & (c)
- 4.** Reverse osmosis process is also called as. [ c ]  
**a.** Super filtration                               **b.** hyper filtration  
**c.** Both (a) & (b)                               **d.** Hypo filtration
- 5.** What is the pH range maintained in EDTA method? [ c ]  
**a.** 4-5   **b.** 6-7   **c.** 9-10                                       **d.** 12-14

6. The colour of Stable complex in EDTA method is [ c ]  
**a.** Blue                   **b.** Wine red  
**c.** Colour less           **d.** Purple
7. Which of the chemical are act as Coagulants help in the settling of [ c ]  
**a.** Alum                   **b.**  $\text{Al}_2(\text{SO}_4)_3$   
**c.** Both (a) & (b)      **d.**  $\text{Mg SO}_4$
8. Desalination of water is. [ a ]  
**a.** Removal of  $\text{NaCl}$       **b.** Removal of suspended  
**c.** Removal of gases        **d.** Removal of metals

***Fill in the blanks:***

1. Hardness of water is expressed in equivalents -----.
2. The chemical name of Calgon is -----.
3. Temporary hardness of water can be removed by-----.
4. Anion exchange resins are regenerated by using-----.
5. Convert 10 ppm of hardness of water in to Degree Clark ( $\text{Cl}^\circ$ ) -----.
6. Which Phosphate is used for treating of too alkaline water -----.
7. Temporary hardness is caused by ----- salts.
8. Cation Exchange resins are regenerated by using-----.

**ELECTROCHEMISTRY**

**Concept of electrochemistry:** The branch of science which deals with the relationship between electrical energy and chemical energy and their inter-conversion of one form to another is called electrochemistry.

**Electrolysis:** The changes in which electrical energy causes chemical reaction to occur.

**Electro chemical cells:** The changes in which electrical energy is produced as a result of chemical change.

**Conductors:** The substances which allow the passage of electric current are called conductors.

Eg. Metals like Cu, Ag, Sn etc.

**Insulators:** The substances which do not allow the electric current to pass through them are called non-conductors or insulators. Eg. Rubber, wood, wax, wool, glass etc.

**Metallic conductors:** These are the metallic substances which allow the electric current to pass through them without undergoing any chemical change. The flow of electric current in metallic conductors is due the flow of electrons in the metal atoms. Eg. Metals like Cu, Ag, Sn etc.

**Electrolytes:** These are the substances which allow the electric current to pass through them in their molten states or in the form of their aqueous solutions and undergo chemical decomposition. The flow of electric current through an electrolytic solution is called electrolytic conduction in which charge is carried by ions. These substances do not conduct electricity in the solid state but conduct electricity in the molten state or aqueous solutions due to movement of ions. Eg. Acids, bases and salts.

**Non-electrolytes:** The substances which do not conduct electricity either in their molten state or through their aqueous solutions are called non-electrolytes. Eg. Sugar, glucose, urea, ethyl alcohol etc.

**Strong electrolytes:** The electrolytes which are almost completely dissociated into ions in are called strong electrolytes. Eg: NaCl, KCl, HCl, NaOH, NH<sub>4</sub>NO<sub>3</sub>

**Weak electrolytes:** The electrolytes which do not ionize completely in solution are called weak electrolytes. Equilibrium is established between unionized electrolyte and the ions formed in the solution.

**Summary**

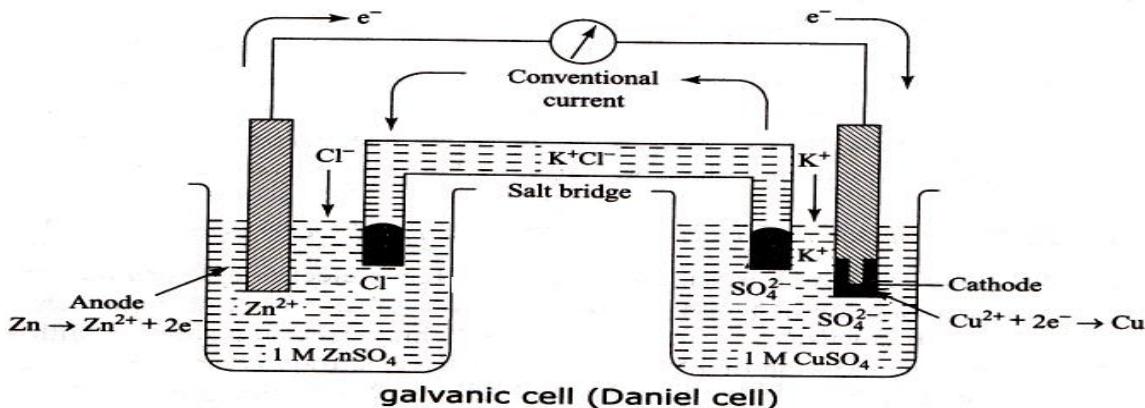
Sl.No.	Parameter	Notation	Formula	Units
1.	Resistance	R	$R = \rho \left( \frac{1}{a} \right)$	Ohms ( $\Omega$ )
2.	Specific resistance	P	$\rho = R \left( \frac{a}{1} \right)$	Ohm.cm
3.	Conductance	C	$C = \frac{1}{R}$	Ohm <sup>-1</sup>
4.	Specific conductance	K	$\kappa = \frac{1}{R} \left( \frac{1}{a} \right)$	ohm <sup>-1</sup> . cm <sup>-1</sup> (or) S. cm <sup>-1</sup>
5.	Equivalent conductance	$\lambda_v$	$\lambda_v = \frac{\kappa \times 1000}{\text{Normality}}$	Ohm <sup>-1</sup> . cm <sup>2</sup> . equiv <sup>-1</sup>
6.	Molar conductance	$\lambda_m$	$\lambda_m = \frac{\kappa \times 1000}{\text{Molarity}}$	Ohm <sup>-1</sup> . cm <sup>2</sup> . mole <sup>-1</sup>
7.	Cell constant	X	l/a	cm <sup>-1</sup>

**ELECTRO CHEMICAL CELLS**

- An electrochemical cell is a device which converts chemical energy into electrical energy.
- The redox reaction is utilized for generation of electrical energy.
- The electrochemical cells are commonly referred as Voltaic or Galvanic cells.
- The electromotive force (EMF) of such cell is directly proportional to intensity of chemical reaction taking place in it.
- The electrochemical cell is divided into two half cells. The half cell electrode where oxidation (loss of electrons) occurs is called anode (negative electrode). The half cell electrode where reduction (gain of electrons) occurs is called cathode (positive electrode). An electrochemical cell is the coupling of these two half cells.

**DANIEL CELL:**

- The Daniel cell is a typical example of Galvanic cell.
- Daniel cell consists of a beaker containing copper rod dipped in  $\text{CuSO}_4$  solution which is connected to another beaker containing zinc rod dipped in  $\text{ZnSO}_4$  solution by a salt bridge.
- Salt bridge is an inverted U-tube containing saturated solution of some electrolyte such as  $\text{KCl}$ ,  $\text{KNO}_3$ ,  $\text{NH}_4\text{NO}_3$  which does not undergo chemical change during the process. The saturated solution is generally taken in agar-agar jelly or gelatin.
- The salt bridge allows the flow of ions to pass through it when the flow of electric current takes place. It completes the electrical circuit and maintains the electrical neutrality of two half cell solutions.

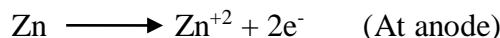


- When the circuit is completed, electric current flows through the external circuit as indicated by an ammeter. The following observations are made:
  1. Zinc rod gradually loses its weight.
  2. The concentration of  $\text{Zn}^{2+}(aq)$  in the  $\text{ZnSO}_4(aq)$  solution increases.
  3. Copper gets deposited on the electrode.
  4. The concentration of  $\text{Cu}^{2+}(aq)$  in  $\text{CuSO}_4(aq)$  solution decreases.
  5. The flow of electrons is from Zn-electrode (anode) to Cu-electrode (cathode).
  6. The flow of electric current is from Cu-electrode (cathode) to Zn-electrode (anode).

**The above observations can be explained as follows:**

## UNIT-III

- Zn is oxidized to  $Zn^{+2}$  ions which go in the solution and therefore Zn rod gradually loses its weight (oxidation half cell).



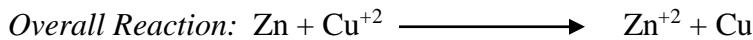
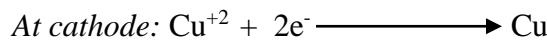
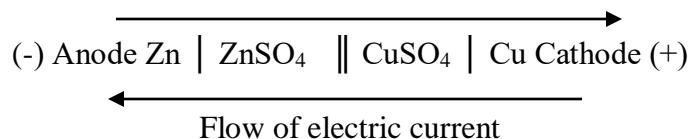
- The electrons released at the Zn electrode move towards Cu electrode through external circuit.  
➤ These electrons are accepted by the  $Cu^{+2}$  ions in the solution and get reduced to copper which gets deposited on the Cu-electrode (reduction half cell).



- The oxidation of Zn occurs at anode (negative terminal) and reduction of  $Cu^{+2}$  occurs at cathode (positive terminal).

- The flow of electrons is from negative terminal (anode) to positive terminal (cathode).

Flow of electrons



### TYPES OF ELECTRODES

**Electrode potential (or) Single Electrode potential ( $E$ ):** It is the measure of tendency of a metallic electrode to lose or gain electrons, when it is in contact with a solution of its own salt.

**Standard Electrode potential ( $E^\circ$ ):** It is the measure of tendency of a metallic electrode to lose or gain electrons, when it is in contact with a solution of its own salt of one molar concentration at  $25^\circ C$ .

**Types of Electrodes:** An electrochemical cell consists of two electrodes, positive and negative. Each electrode constitutes a half cell or a single electrode.

### CONSTRUCTION AND FUNCTIONING OF SOME STANDARD ELECTRODES:

The single electrode potential is conveniently measured by combining the half cell with a standard electrode and measuring the total EMF of the cell.

$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}}$$

$$E_{\text{cell}} = E_{\text{right}} - E^\circ \text{ (if standard electrode is anode)}$$

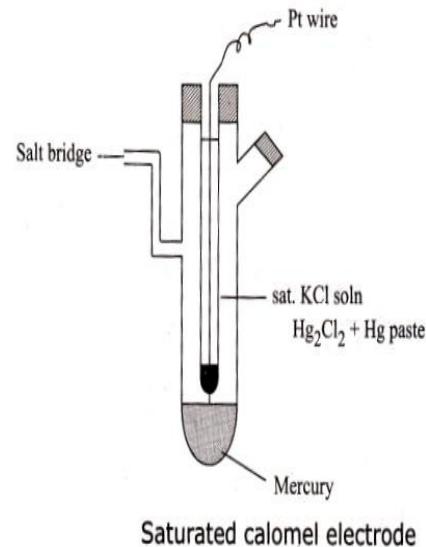
$$E_{\text{cell}} = E^\circ - E_{\text{left}} \text{ (if standard electrode is cathode)}$$

Where  $E^\circ$  is the standard electrode potential.

Eg. Standard hydrogen electrode, Calomel electrode, Quinhydrone electrode

## 1. CALOMEL ELECTRODE

- It is a secondary reference electrode.
- It is a mercury-mercurous chloride ( $Hg-Hg_2Cl_2$ ) electrode.
- The calomel electrode is used as only reducing electrode *i.e.* as cathode only.
- It consists of a glass tube having a side tube on each side. One side tube acts as salt bridge and other is used to fill KCl solution.
- The high purity mercury is placed at the tip of this tube and connected to the circuit by the means of Pt-wire, sealed in a glass tube.
- The surface of Hg is covered with a paste of mercurous chloride (calomel) and Hg in KCl solution.
- The electrolyte is the solution of KCl.
- The electrode is connected with the help of side tube on the left through salt bridge with the other electrode whose potential has to be determined.
- The potential of the calomel electrode depends upon the concentration of KCl.



Concentration of KCl	0.1N	1.0N	Saturated
Electrode potential (V)	0.3335	0.2810	0.2422

**Representation of calomel electrode:**  $Hg, Hg_2Cl_{(s)} \mid KCl$  (saturated solution)

## 2. ION SELECTIVE ELECTRODE- GLASS ELECTRODE

- They possess an ability to respond to only certain specific ions thereby developing a potential with respect to that species only in a given mixture and ignore all the other ions totally.
- The potential developed by ion selective electrode depends on the concentration of specific ion of interest.
- Eg. Glass electrode specific for  $H^+$  ions and pressed pallet of  $Ag_2S + AgCl$  specific for  $Cl^-$  ions.

### **GLASS ELECTRODE:**

- When two solutions of different pH values are separated by a thin glass membrane, a potential difference develops between the two surfaces of the membrane.
- This potential difference developed is proportional to the difference in pH value.
- The glass membrane functions as ion-exchange resin.

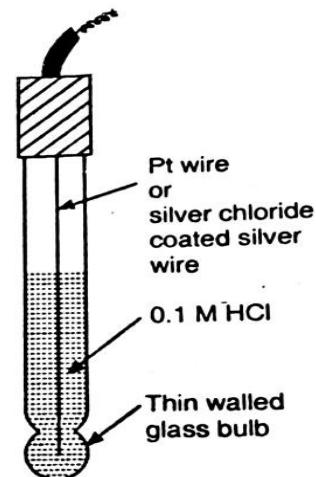
## UNIT-III

- An equilibrium is established between  $\text{Na}^+$  ions of the glass and  $\text{H}^+$  ions in the solution.
- The potential of the glass electrode is given by:

$$E_G = E^{\circ}_G + 0.0592 \text{ pH}$$

- Where pH range of the test solution is between 1-10.
- The glass electrode consists of a thin walled glass tube containing  $\text{AgCl}$  coated Ag-electrode or simply Pt-electrode in 0.1M HCl.

**Cell representation of glass electrode is given by:**



**Glass electrode & determination of pH by glass electrode:**

- HCl in the bulb furnishes constant  $\text{H}^+$  ion concentration. Thus it is Ag-AgCl electrode reversible with respect to  $\text{Cl}^-$  ions.
- It is used as internal reference electrode for determining the pH of the solution especially the colored solution containing oxidizing or reducing agents.

**Determination of pH of unknown solution by glass electrode:**

- In order to determine the pH of the solution, the glass electrode is placed in the test solution. This half cell is coupled with saturated calomel electrode and the EMF of the cell is measured.

- **Cell representation:**  $\text{Pt}, \text{HCl} (0.1\text{M}) \mid \text{Glass} \parallel \text{KCl}$   
 $(\text{sat}) \text{Hg}_2\text{Cl}_{2(s)} \mid \text{Hg}$

$$E_{\text{Cell}} = E^{\circ}_{\text{Calomel}} - E^{\circ}_{\text{Glass}}$$

$$E_{\text{Cell}} = 0.2422 - [E^{\circ}_{\text{Glass}} + 0.0592 \text{ pH}]$$

$$E_{\text{Cell}} = \frac{0.2422 - E_{\text{Cell}} - E^{\circ}_{\text{Glass}}}{0.0592}$$

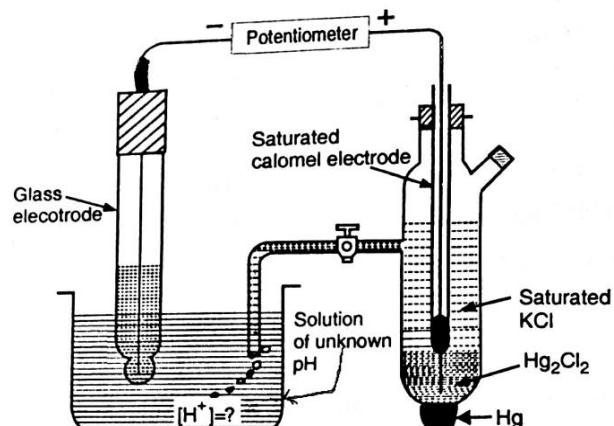
- Since the resistance is very high, a special electron tube voltmeter is used to measure the EMF of the above cell.

**Advantages:**

1. It is simple and can be easily used.
2. The results are accurate.
3. Equilibrium is rapidly reached.

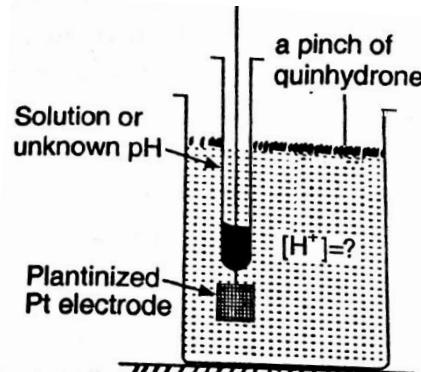
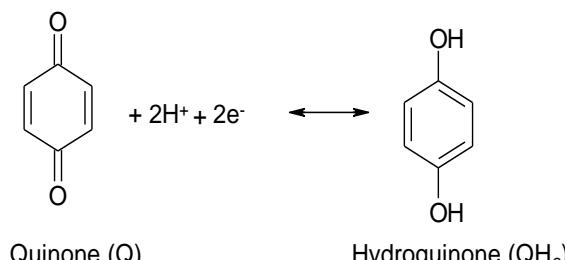
**Limitations:**

1. The range of solution pH is between 1 to 10.
2. The resistance of the membrane is very high.



**3. QUINHYDRONE ELECTRODE**

- It is a Quinone-hydroquinone system which forms a reversible redox system.
- When a Pt-electrode is immersed in this system, the potential E developed is given by



$$E_Q = E_Q^\circ - \frac{2.303RT}{nF} \log_{10} \frac{[\text{QH}_2]}{[\text{Q}][\text{H}^+]^2}$$

- When Quinone and Hydroquinone are maintained at equi molar ratios, then pH of an unknown solution can be determined using this electrode.
- The electrode potential of Quinhydrone electrode depends upon concentration of  $\text{H}^+$  ions which can be used for the determination of pH of unknown solution.
- A pinch of quinhydrone powder which is sparingly soluble solid is added to the experimental solution with stirring until the solution is saturated.

**Determination of pH of unknown solution by Quinhydrone electrode:**

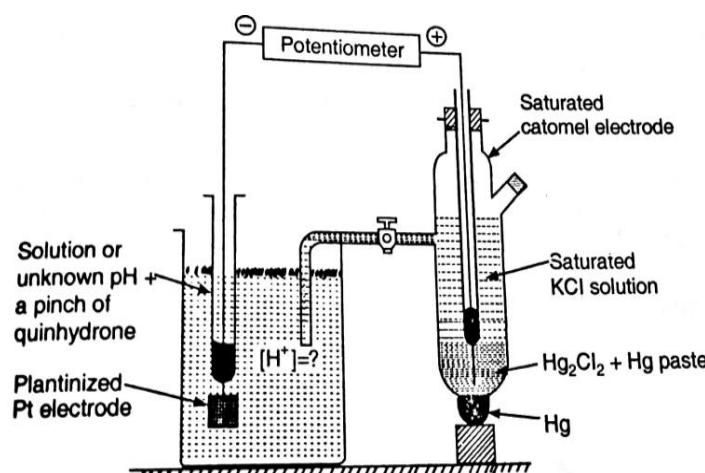
- **Cell representation:**  $\text{Pt}, \text{QH}_2 \mid \text{Q}, \text{H}^+(\text{?}) \parallel \text{KCl (saturated)} \text{ Hg}_2\text{Cl}_2 \mid \text{Hg}$

- A Pt-electrode is inserted into the solution and a pinch of quinhydrone is added.
- This half cell is connected to a saturated electrode calomel electrode and the EMF of the solution is determined potentiometrically.

$$E_{\text{Cell}} = E_{\text{Calomel}} - E_{\text{Quinhydrone}}$$

$$E_{\text{Cell}} = 0.2422 - (0.6994 - 0.0592 \text{pH})$$

$$\text{pH} = \frac{E_{\text{Cell}} - 0.4572}{0.0592}$$



**Advantages:**

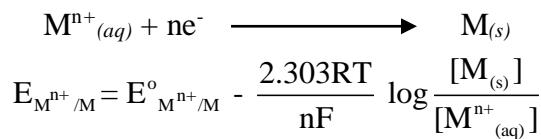
1. It is useful in acid-base titrations.
2. Equilibrium is rapidly attained.
3. It can be used for many metal ions which usually effect hydrogen electrode.

## UNIT-III

### NERNST EQUATION

Standard electrode potentials are measured at standard states i.e at 1M concentration of electrolyte, temperature at 298 K and 1atm pressure. However the electrode potentials depend upon concentration of electrolyte solutions and temperature. Nernst equation gives the relationship between electrode potentials and concentration of electrolytic solutions.

➤ For the general reduction reaction occurring at an electrode,



Where  $E^{\circ}$  = Standard EMF of the cell for 1 M solution at 298 K;

R = Gas constant;

T = Kelvin temperature;

n = number of electrons involved in the cell reaction;

F = Faraday of electricity;

E = electrode potential of the metal;

[M] = activity of metal in the metal phase and is taken as unity;

$[\text{M}^{n+}]$  = activity of metal ions in the solution is taken equal to their molarities;

But at STP conditions, R = 8.314JK<sup>-1</sup>mol<sup>-1</sup>; T = 298K; F = 96500 coulomb charge. Then the Nernst equation becomes

$$\text{E}_{\text{M}^{n+}/\text{M}} = \text{E}^{\circ}_{\text{M}^{n+}/\text{M}} - \frac{2.303 \times 8.314 \times 298}{n \times 96500} \log \frac{1}{[\text{M}^{n+}_{(aq)}]} \quad \text{considering } [\text{M}^{n+}_{(s)}] = 1$$

$$\text{E}_{\text{M}^{n+}/\text{M}} = \text{E}^{\circ}_{\text{M}^{n+}/\text{M}} - \frac{0.0592}{n} \log \frac{1}{[\text{M}^{n+}_{(aq)}]}$$

$$\text{E}_{\text{M}^{n+}/\text{M}} = \text{E}^{\circ}_{\text{M}^{n+}/\text{M}} + \frac{0.0592}{n} \log [\text{M}^{n+}]$$

**Nernst equation enables us to calculate the following:**

1. Half cell potential or single electrode potential.
2. Cell potential or EMF of the cell.
3. Equilibrium constant for the cell reaction.

### ELECTROCHEMICAL SERIES AND ITS APPLICATIONS

When the various electrodes (metals) are arranged in the order of their increasing values of standard reduction potential on the hydrogen scale, then the arrangement is called electrochemical series.

# UNIT-III

(or)

When the various electrodes (metals) are arranged in the order of their decreasing values of standard oxidation potential on the hydrogen scale, then the arrangement is called electrochemical series.

Electrode	Electrode reaction	$E^\circ$ , volts	Nature
Li <sup>+</sup> /Li	$\text{Li}^+ + \text{e}^- \longleftrightarrow \text{Li}$	-3.01	Anodic ↑
Mg <sup>2+</sup> / Mg	$\text{Mg}^{2+} + 2\text{e}^- \longleftrightarrow \text{Mg}$	-2.37	
Zn <sup>2+</sup> / Zn	$\text{Zn}^{2+} + 2\text{e}^- \longleftrightarrow \text{Zn}$	-0.76	
Fe <sup>2+</sup> / Fe	$\text{Fe}^{2+} + 2\text{e}^- \longleftrightarrow \text{Fe}$	-0.44	
Sn <sup>2+</sup> / Sn	$\text{Sn}^{2+} + 2\text{e}^- \longleftrightarrow \text{Sn}$	-0.136	
Pb <sup>2+</sup> / Pb	$\text{Pb}^{2+} + 2\text{e}^- \longleftrightarrow \text{Pb}$	-0.13	
H <sup>+</sup> / H <sub>2</sub>	$2\text{H}^+ + 2\text{e}^- \longleftrightarrow \text{H}_2$	0.00	Pt-reference
Cu <sup>2+</sup> / Cu	$\text{Cu}^{2+} + 2\text{e}^- \longleftrightarrow \text{Cu}$	+0.34	↓ Cathodic
Ag <sup>+</sup> / Ag	$\text{Ag}^+ + \text{e}^- \longleftrightarrow \text{Ag}^+$	+0.80	
Au <sup>+</sup> / Au	$\text{Au}^+ + \text{e}^- \longleftrightarrow \text{Au}^+$	+1.50	
1/2F <sub>2</sub> / F <sup>-</sup>	$1/2\text{F}_2 + \text{e}^- \longleftrightarrow \text{F}^-$	+2.87	

### Applications of electrochemical series:

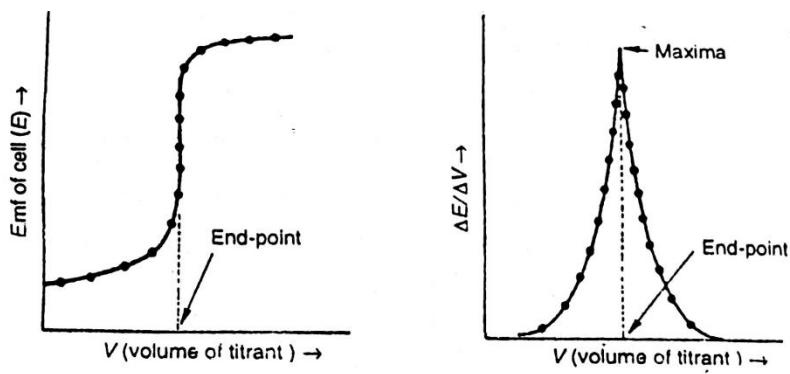
1. Calculation of standard EMF of the cell.
2. Relative ease of oxidation (or) Reduction.
3. Displacement of one element by the other.
4. Hydrogen displacement behavior.
5. Corrosion tendency of the elements.

### POTENTIOMETRIC TITRATIONS

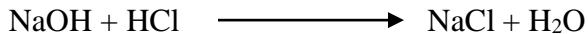
The titration in which the equivalent (or) end point of a reaction is determined with the help of measurement of the potentials of the reaction mixture is known as potentiometric titration.

#### 1. Acid-Base Titrations:

The acid solution whose strength has to be determined is taken in a beaker and the hydrogen electrode and calomel electrode were dipped in the solution. The electrodes are connected to the potentiometer and the EMF is measured. A known volume of standard alkali solution is added from a burette, stirred thoroughly and the EMF of the cell is recorded. Like this 10-15 readings are recorded by repeating the procedure of the addition of alkali. The volume of alkali



added is plotted against EMF observed. The steepest portion of the curve indicates the equivalent point of the titration.



## 2. Redox titrations:

The EMF of the electrode is determined by the activity of ratio of the substance being oxidized or reduced. For example  $\text{Fe}^{+2}$  titrated against  $\text{K}_2\text{Cr}_2\text{O}_7$ . Ferrous iron solution is taken in the beaker and treated with dil.  $\text{H}_2\text{SO}_4$ . Platinum electrode and calomel electrode are dipped into the solution and they are connected to the potentiometer. The EMF of the solution after the addition of  $\text{K}_2\text{Cr}_2\text{O}_7$  from burette is recorded. A graph is plotted with EMF and volume of  $\text{K}_2\text{Cr}_2\text{O}_7$ . The steep rise is the end point of the titration.

## 3. Precipitation reactions:

The EMF of the electrode is determined by the precipitation of product. For example, titration of  $\text{AgNO}_3$  with  $\text{KCl}$  where the later precipitates out.  $\text{KCl}$  is used along with calomel electrode.  $\text{AgNO}_3$  is taken in the burette and  $\text{KCl}$  is taken in the beaker containing electrodes. The EMF of the cell is measured and plotted against volume of silver nitrate added. The steep rise in the curve shows the end point of the titration.



### Advantages:

1. Colored solutions where the use of indicator is impossible are estimated by potentiometric titrations.
2. Solutions more than one halide can be analyzed in a single titration against silver nitrate.

**BATTERIES**

- The term battery is generally used for two or more galvanic cells connected in series. Thus a battery is a series of portable electrochemical cells which are capable of generating electrical energy.
- Batteries are of three types: (1) Primary cell (2) Secondary cell (3) Fuel cell.

**Applications of batteries:**

- The portability of electronic equipments in the form of handsets has been made possible by batteries.
- A variety of electronic gadgets with more reliability and service have been made more useful with the introduction of rechargeable storage batteries.

**COMPARISON BETWEEN PRIMARY AND SECONDARY CELLS**

<b>Sl. No.</b>	<b>Primary cells</b>	<b>Secondary cells</b>
<b>1.</b>	Cell reaction is irreversible	Cell reaction is reversible.
<b>2.</b>	Must be discarded after use.	May be recharged.
<b>3.</b>	Have relatively short shelf life.	Have long shelf life.
<b>4.</b>	Function only as galvanic cells.	Functions both galvanic Cell & as electrolytic cell.
<b>5.</b>	They cannot be used as storage devices	They can be used as energy storage devices (e.g. solar/ thermal energy converted to electrical energy)
<b>6.</b>	They cannot be recharged	They can be recharged.
<b>7.</b>	Eg. Dry cell, Alkaline cell and Li-battery.	Eg. Lead acid storage cell, Ni-Cd battery.

**PRIMARY BATTERIES**

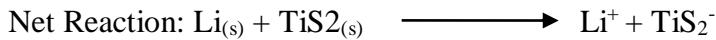
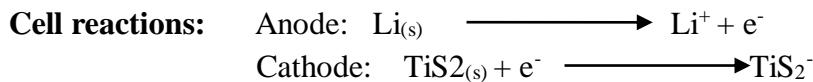
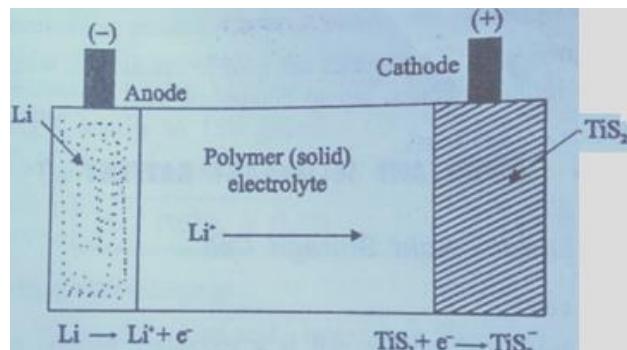
- The cell reaction is not reversible.
- No electricity is produced after complete conversion of the reactants to products and the cell becomes dead.
- These batteries are used as source of DC power.
- Eg. Lithium cell, Dry cell (Leclanche cell) and Alkaline cells

**LITHIUM CELL - PRIMARY BATTERY**

- Lithium cell is a primary cell, Lithium metal acts as anode.
- Metal oxide or  $TiS_2$  acts as cathode.
- Solid polymer will act as an electrolyte; this polymer is packed in between the electrodes. The electrolyte permits the passage of ions but not that of electrons.

## UNIT-III

- The EMF of the cell is 3.0V



### Advantages:

1. In this cell voltage is high, 3.0V.
2. Lithium is a light weight metal (7gms).
3. Lithium has the most negative  $E^\circ$  value.
3. In Lithium cell all constituents are in solid form so that there is no leakage.
4. The battery can be made in a variety of sizes and shapes.

### Applications:

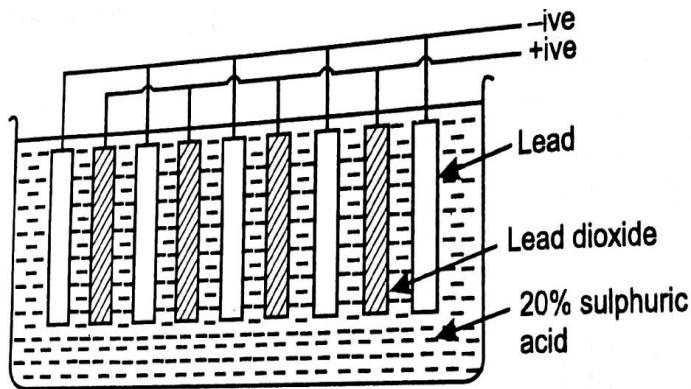
1. Button sized Lithium batteries are used in calculators, watches, cameras, mobile phones, laptop computers, etc.,

## **SECONDARY BATTERIES**

- The cells in which the cell reaction is reversed by passing direct current in opposite direction i.e. it can operate both as a voltaic cell and as an electrolytic cell.
- The secondary batteries can be used through a large number of cycles of discharging and charging. They are used as a source of DC power.  
Eg. Lead –acid storage cell, Lithium ion batteries and Ni-Cd battery.

### **1. LEAD ACID STORAGE CELL - SECONDARY BATTERY**

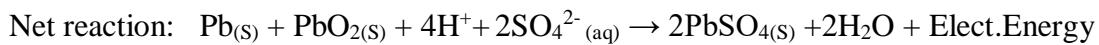
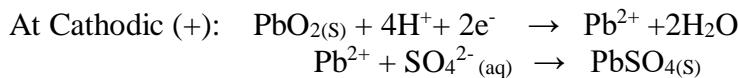
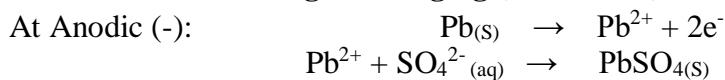
- It consists of lead –antimony alloy coated with lead dioxide ( $\text{PbO}_2$ ) as cathode and spongy lead as anode. The electrolyte is a 20% solution of  $\text{H}_2\text{SO}_4$ .
- The storage cell can operate both as voltaic cell and electrolytic cell.
- It acts as voltaic cell when supplying energy and as a result eventually becomes rundown.
- The cell operates as electrolytic cell when being recharged.



➤ The cell consists of a series of Pb-plates (negative plates) and PbO<sub>2</sub> plates (positive plates) connected in parallel. The plates are separated from adjacent one by insulators like wood, rubber or glass fiber.

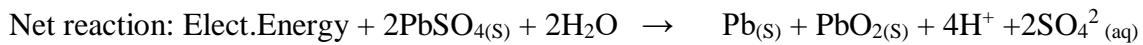
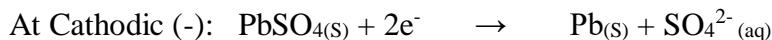
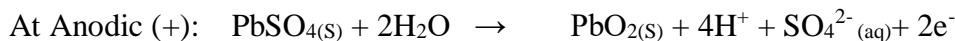
➤

**➤ Cell reactions during discharging (voltaic cell):**



During the discharging the battery, H<sub>2</sub>SO<sub>4</sub> is consumed the density of H<sub>2</sub>SO<sub>4</sub> falls to 1.20g/cm<sup>3</sup>, then battery needs recharging. In discharging, the cell acts as a voltaic cell where oxidation of lead occurs. In charging, the cell is operated like an electrolyte cell and electric energy is supplied to it.

**➤ Cell reactions during recharging (electrolytic cell):**



During this process, lead is deposited at the cathode, PbO<sub>2</sub>, is formed at the anode and H<sub>2</sub>SO<sub>4</sub> is regenerated in the cell.

**Applications:** The lead storage cells are used to supply current for electrical vehicles, gas engine ignition, telephone exchanges, electric trains, mines, laboratories, hospitals, broadcasting stations, automobiles and power station.

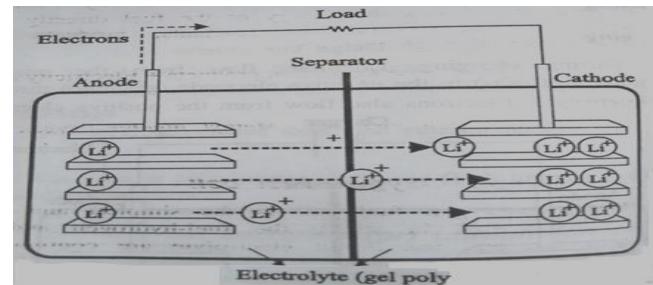
## 2. LITHIUM ION CELL - SECONDARY BATTERY

➤ It is rechargeable secondary cell. In lithium battery consists of a layers of porous carbon acts as anode and layers of lithium metal oxide acts as cathode.

➤ Electrolytes, generally a polymer gel, act as separator between the electrodes. The separator permits the passage of ions but not that of electrons.

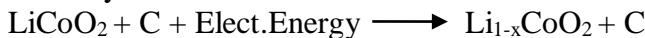
**Cell reactions during discharging** (voltaic cell): During discharging, the  $\text{Li}^+$  ions flow back through the electrolyte from negative electrode to the positive electrode.

Electrons flow from the negative electrode to the positive electrode. The  $\text{Li}^+$  ions and electrons combine at the positive electrode and deposit there as Li.



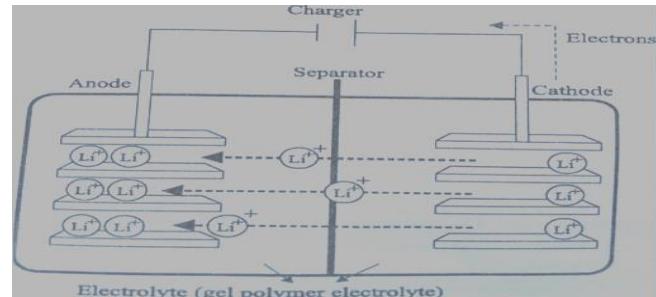
**Cell reactions during charging** (electrolytic cell):

During charging, the  $\text{Li}^+$  ions flow from the positive electrode to negative electrode through electrolyte.



### Advantages:

1. Lithium –ion batteries are high voltage and light weight batteries.
2. It is smaller in size.
3. It produces three times the voltage of Ni-Cd batteries.



### Applications:

1. It is used in cell phone, note PC, portable LCD TV, semiconductor driven audios.

## **UNIT-III**

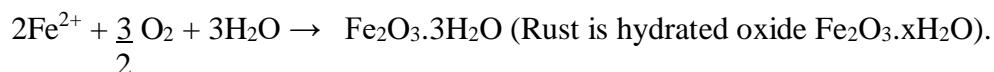
## **CORROSION AND ITS CONTROL.**

**Definition:** Corrosion may be defined as the disintegration or eating away of a metallic material from its surface by chemical or electrochemical reaction with its environment.

### Corrosion (Oxidation)

Metal  $\xrightarrow{\text{Metallurgy (Reduction)}}$  Metallic compound + energy

**Example:** Rusting of iron when exposed to atmospheric conditions.



## **CAUSES OF CORROSION**

In nature metals have a natural tendency to revert back to combined states. During this process mostly oxides are formed though in some cases sulphides, carbonates. Any process of deterioration and loss of solid metallic material by chemical or electrochemical attack by its environment is called corrosion. Corrosion is the reverse process of metallurgy.

Ore → Metal → Corrosion Product  
 (Stable) (Unstable) (Stable)

## **EFFECT OF CORROSION**

- Poor appearance
  - Maintenance and operating costs
  - Plant shutdowns
  - Contamination of product
  - Loss of valuable products due to leakage
  - Effects on safety and reliability in handling hazardous materials
  - Product liability
  - Valuable metallic properties such as conductivity, malleability, ductility, etc. are lost due to corrosion.

**THEORIES OF CORROSION**

There are two theories of corrosion

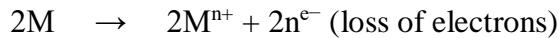
1. Dry/Chemical theory
2. Wet/Electrochemical/galvanic theory

**1. Dry (or) chemical Corrosion:** According to this theory type of corrosion occurs mainly through the direct chemical action of atmospheric gasses ( $O_2$ ,  $H_2S$ ,  $SO_2$ , and  $N_2$ ) with metal.

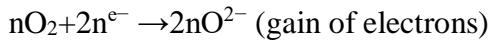
**There are three main types of dry Corrosion:**

- i. Oxidation corrosion
- ii. Corrosion of the other gases
- iii. Liquid metal corrosion.

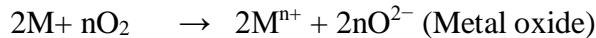
**i. Oxidation corrosion:** This is carried out by the direct action of oxygen low or high temperatures on metals in absence of moisture at ordinary temperature metals are very slightly attacked. The exceptions are Alkali metals and Alkaline earth metals. At high temperature all metals are oxidized. The exception is Ag, Au and Pt.



(Metal ion)



(Oxide ion)



**Mechanism:** During oxidation of a metal, metal oxide is formed as a thin film on the metallic surface which protects the metal from further corrosion. If diffusion of either oxygen or metal is across this layer, further corrosion is possible. Oxides of Pb, Al, Sn are stable, and hence inhibit further corrosion.

**ii. Corrosion of the other gases:**  $Cl_2$ ,  $SO_2$ ,  $H_2S$ ,  $NO_x$  gases react with metal and form corrosion products which may be protective or non-protective. Dry  $Cl_2$  reacts with Ag and forms  $AgCl$  which is a protective layer, while  $SnCl_4$  is volatile in petroleum industries at high temperatures,  $H_2S$  attacks steel forming  $FeS$  scale which is porous and interferes with normal operations.

**iii. Liquid metal corrosion:** In several industries, molten metals pass through metallic pipes and causes corrosion due to dilution or due to internal penetration.

**Example:** Coolant (sodium metal) causes cadmium corrosion in nuclear reactor. Liquid metal mercury dissolves most metals by forming amalgams, thereby corroding them.

## **2. Wet (or) Electrochemical Corrosion:**

This type of Corrosion occurs where a conducting liquid is in contact with the metal (or) when two dissimilar metals (or) alloys are dipped partially in a solution. This corrosion occurs due to the existence of separate anodic and cathodic parts, between which current flows through the conducting solution. At anodic area, oxidation reaction occurs thereby destroying the anodic metal either by dissolution (or) formation of compounds. Hence corrosion always occurs at anodic parts.  $M^{n+}$  dissolution formation of compound at cathodic part, reduction reaction (electro nation) occurs. It does not affect the cathode, since most metals cannot be further reduced. At cathodic part, the dissolved constituents in the conducting medium accept the electrons forming ions ( $OH^-$ ,  $O^{2-}$ ). The metallic ions formed at anodic part and the ions formed at cathodic part diffuse towards each other through conducting medium and form a corrosion product somewhere between anode and cathode.

**Mechanism:** Electrochemical corrosion involves flow of electrons between anode and cathode. The anodic reaction involves dissolution of metal liberating free electrons.

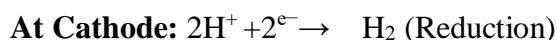


The cathodic reaction consumes electrons with either *evolution of hydrogen* or *absorption of oxygen* which depends on the nature of corrosive environment.

**i. Evolution of hydrogen:** This type of corrosion occurs in acidic medium.

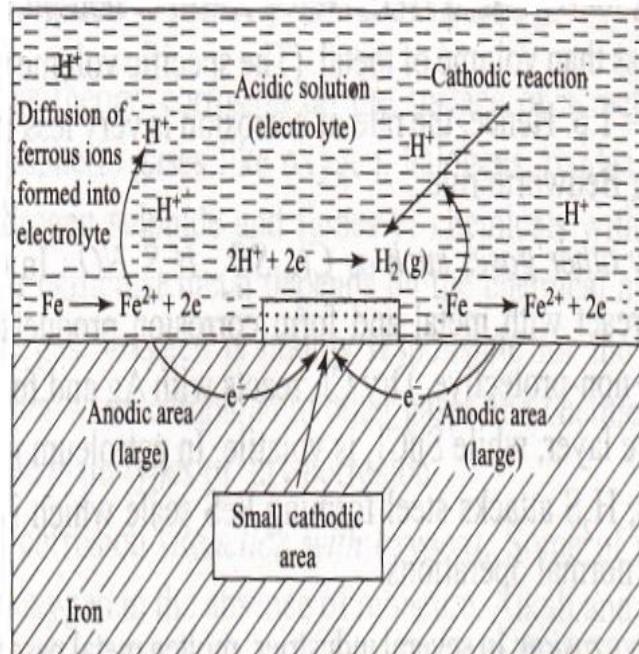
**Ex:** Considering the metal Fe, anodic reaction is dissolution of iron as ferrous ions with liberation of electrons.

The electrons released flow through the metal from anode to cathode, whereas  $H^+$  ions of acidic solution are eliminated as hydrogen gas.



This type of corrosion causes displacement of hydrogen ions from the solution by metal ions. All metals above hydrogen in electrochemical series have a tendency to get dissolved in acidic solution with simultaneous evolution of  $H_2$  gas.

The anodes are large areas, whereas cathodes are small areas.



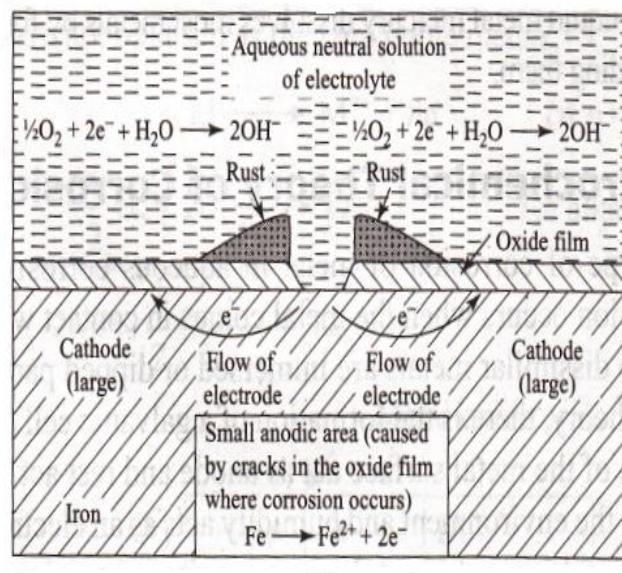
(a)

**ii. Absorption of oxygen:**

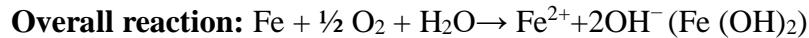
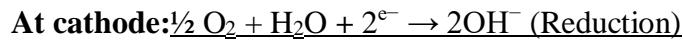
This type of corrosion occurs in neutral (or) basic medium.

**Ex:** Rusting of iron in neutral aqueous solution of electrolytes in presence of atmospheric oxygen.

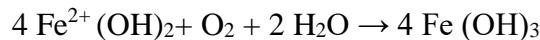
Usually the surface of iron is coated with a thin film of iron oxide. If the film develops cracks, anodic areas are created on the surface. While the metal parts act as cathodes. It shows that anodes are small areas, while the rest metallic part forms large cathodes.



(b)



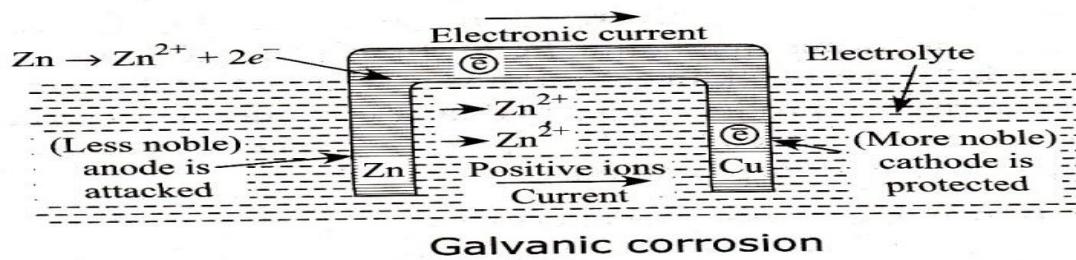
If oxygen is in excess, ferrous hydroxide is easily oxidized to ferric hydroxide.



The product called yellow rust corresponds to  $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ .

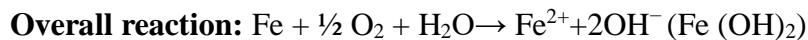
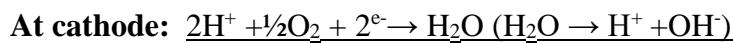
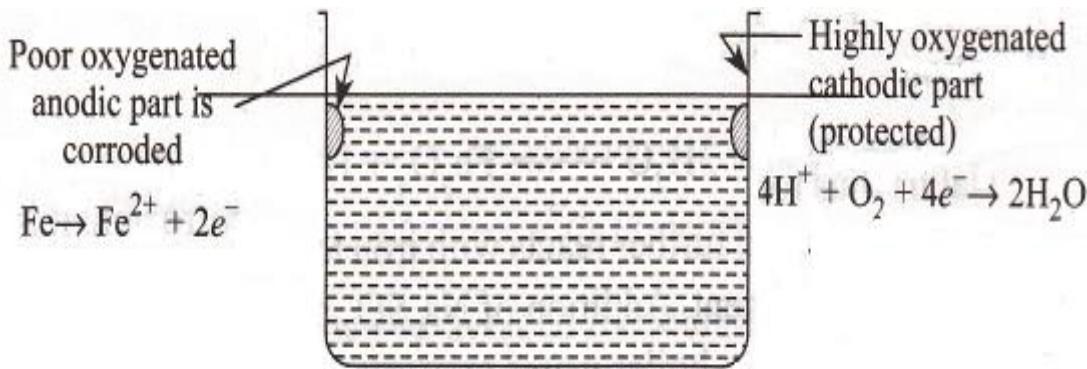
**TYPES OF CORROSION**

**1. Galvanic Corrosion:** When two dissimilar metals are electrically connected and exposed to an electrolyte, the metal higher in electrochemical series undergoes corrosion. This type of corrosion is called galvanic corrosion.



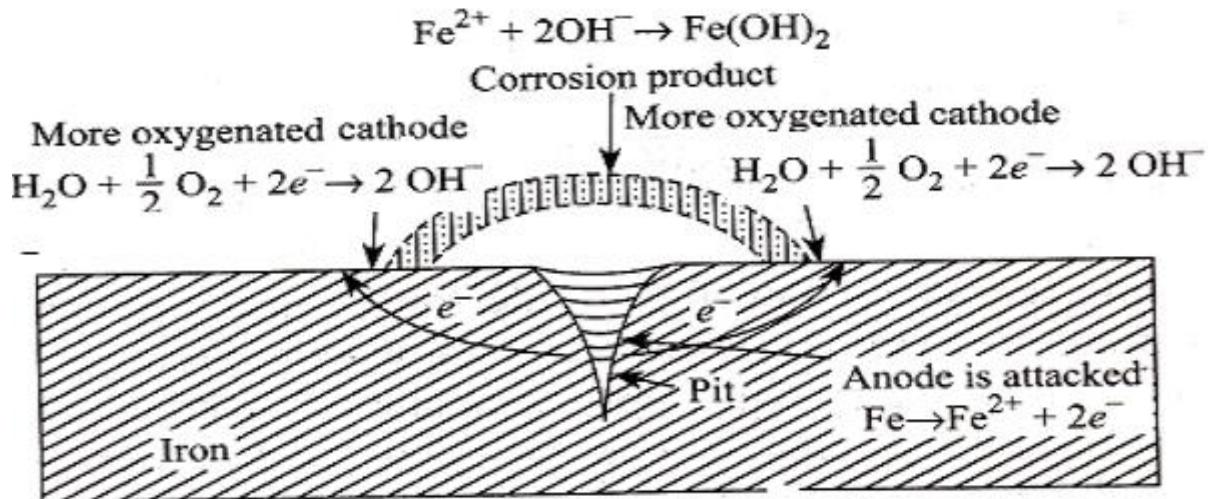
Galvanic corrosion can be avoided by coupling metals close to the electrochemical series, fixing insulating material between two metals, by using larger anodic metal and smaller cathodic metal.

**2. Waterline Corrosion:** This is also known as *differential oxygen concentration corrosion*. It has been observed in the case of iron tank containing water, that the portion of iron tank just below the water level undergoes corrosion. It is due to the difference in oxygen concentration.



The area above the waterline (highly oxygenated) acts as cathodic and is not affected by corrosion. However, if the water is relatively free from acidity, little corrosion occurs. This type of corrosion is prevented to a great extent by painting the sides of the ships by antifouling paints.

**3. Pitting corrosion:** Pitting corrosion is due to crack on the surface of a metal, there is a formation of a “*local galvanic cell*” (Pinholes, pits and cavities) in the metal.



Pitting is usually the result of the breakdown or cracking of the protective film on a metal at specific points. This gives rise to the formation of small anodic and large cathodic areas. In the corrosive environment this produces corrosion current.

## FACTORS AFFECTING OF CORROSION

The rate and extent of corrosion depends on the nature of the metal and nature of corroding environment.

Those are **1. Effect of metal**

**2. Effect of environment**

**1. Effect of metal:** Different properties of a metal are responsible for corrosion. These properties are given below.

a. Position of metal in galvanic series  
c. Nature of surface/oxide film

b. Hydrogen over voltage  
d. Volatility of corrosion product

**a. Position of metal in galvanic series:** It decides the corrosion rate. A metal having higher position in galvanic series undergoes corrosion when connected to another metal below it.

**b. Hydrogen over voltage:** In case of Zinc metal placed in a normal solution of  $H_2SO_4$ , reaction takes place forming bubbles of hydrogen gas on zinc surface. The process is slow due to high overvoltage of zinc metal (0.7 V) which reduces the effective potential to a small value. In presence of  $CuSO_4$  the corrosion rate of zinc is accelerated.

**c. Nature of surface/oxide film:** In aerated atmosphere, all metals get covered with a thin surface film of metal oxides. The ratio of the volumes of metal oxides to the metal is known as specific volume ratio. Greater is this value lesser is the oxidation corrosion rate. Specific volume ratios of Ni, Cr and W are 1.6, 2.0 and 3.6 respectively suggesting Tungsten has least corrosion. Further the corrosion depends on nature of oxide film. Metals like Al have a firm oxide film in comparison to Fe and hence Al in less corrosive means it follows **Pilling-Bed worth Rule**. The iron oxide is porous in nature and this leads to extension of corrosion to inner surface.

**d. Volatility of corrosion products:** If the corrosion product is volatile, then the underlying surface is exposed for further attack. This causes rapid and continuous corrosion. E.g.  $MoO_3$  is volatile.

**2. Effect of environment:** Different properties of an environment are responsible for corrosion. These properties are given below.

a. Effect of pH  
c. Humidity of air

b. Temperature

**a. Effect of pH:**

In the corrosion reaction described  $H^+$  or  $OH^-$  are also involved. Therefore the effect of pH is obvious. It can be easily seen from the chemical equation for a reaction the direction in which it will shift by change in concentration of  $H^+$  or  $OH^-$ . As a general rule, acids are more corrosive than neutral or alkaline solutions.

## b. Temperature:

As the temperature of environment is increased the reaction rate is increased thereby accelerating corrosion. The effect of temperature on the corrosion rate is complicated because of the fact that it affects the various factors in different ways. The rate of chemical reaction increases, with rise in temperature but the solubility of gases, like oxygen which affect corrosion, decreases. The temperature may affect the protective coatings in different ways. In general, the rate of corrosion due to oxygen or oxidizing agents is decreased with rise in temperature but the rate of hydrogen type corrosion is increased.

## c. Humidity of air:

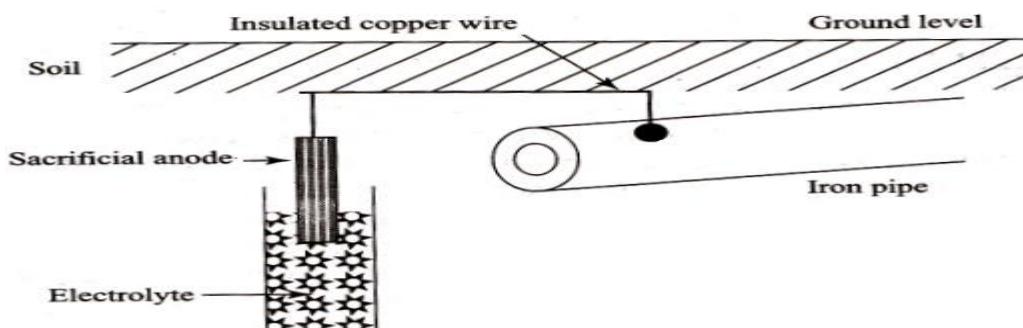
Corrosion of a metal is furnished in humid atmosphere because gases ( $\text{CO}_2$ ,  $\text{O}_2$ ) and vapours present in atmosphere furnish water to the electrolyte essential to establish an electrochemical corrosion cell. The oxide film on the metal surface has the property to absorb moisture. In presence of this absorbed moisture, corrosion rate is enhanced. Rain water may also wash away the oxide film from the metal surface. This leads to enhanced atmospheric attack. The exceptions are Cr, Al.

## **CORROSION CONTROL METHODS**

**1. Cathodic Protection:** The cathodic protection of metals is used to control corrosion metals where it is impossibly to alter the nature of the corrosion medium. The principle involved in this method is to protect metals and alloys from corrosion by making them completely cathodic. Since there will not be any anodic area on the metal, therefore corrosion does not occur. The following are **two types** of cathodic protections.

- a. Sacrificial anodic protection    b. Impressed current cathodic protection

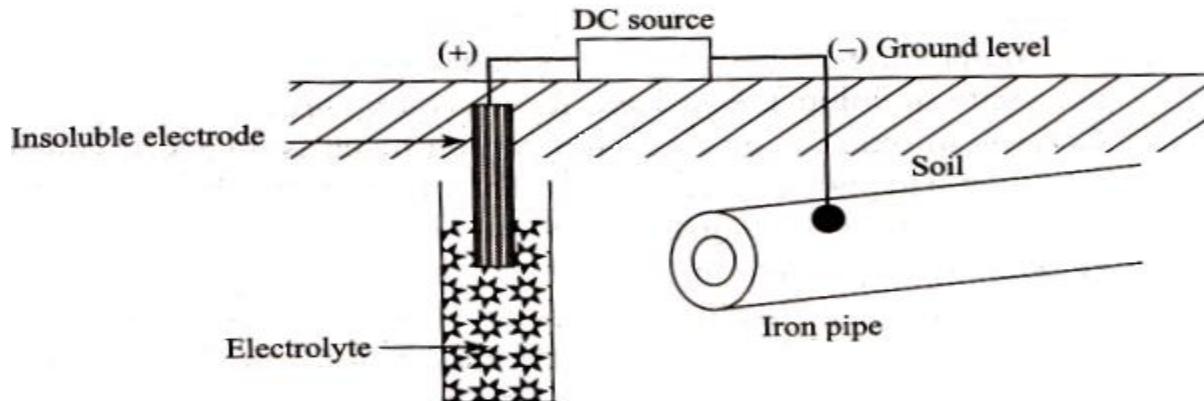
**a. Sacrificial anodic protection:** In this method, the metal structure can be protected from corrosion by connecting it with wire to a more anodic metal. As this more active metal is sacrificed in the process of saving metal from corrosion, it is known as sacrificial anode. The metals which are commonly used as sacrificial anodes are Mg, Zn, Al and their alloys.



**The important applications of this method are:**

- Protection of underground cables and pipelines from soil corrosion.
- Protection of ships and boat hulls from marine corrosion.
- Prevention of rusty water by inserting Mg sheets or rods into domestic water boilers or tanks.

**b. Impressed current cathodic protection:** As the name implies, an impressed current is applied to convert the corroding metal from anode to cathode. The applied current is in opposite direction since to nullify the corrosion current. This can be accomplished by applying sufficient amount of direct current source like battery or rectifier to an anode like graphite, high silica iron, stainless steel or platinum buried in the soil or immersed in the corrosion medium, and connected to the corroding metal structure which is to be protected as shown in the diagram below.



In impressed current cathodic protection, electrons are supplied from an external cell, so that the object itself becomes cathodic and not oxidized. This type of cathodic protection has been applied to buried structures such as tanks and pipelines, transmission line-towers, marine piers, laid-up ships etc. since, their operating and maintenance costs are less, they are well suited for large structures and long term operations.

**2. Surface coatings/ Metallic coatings:** These are produced by coating one metal on the surface of molten metal. The metal which is protected is called base metal and the metal which is coated on the surface of the base metal is called coating metal.

**Methods of Application of Metallic coatings:** Metallic coatings are done by the following methods:

- |                          |                                 |
|--------------------------|---------------------------------|
| <b>I: Hot dipping.</b>   | <b>II: Electroplating.</b>      |
| <b>III. Anodization.</b> | <b>IV. Electroless Plating.</b> |

### **I. HOT DIPPING**

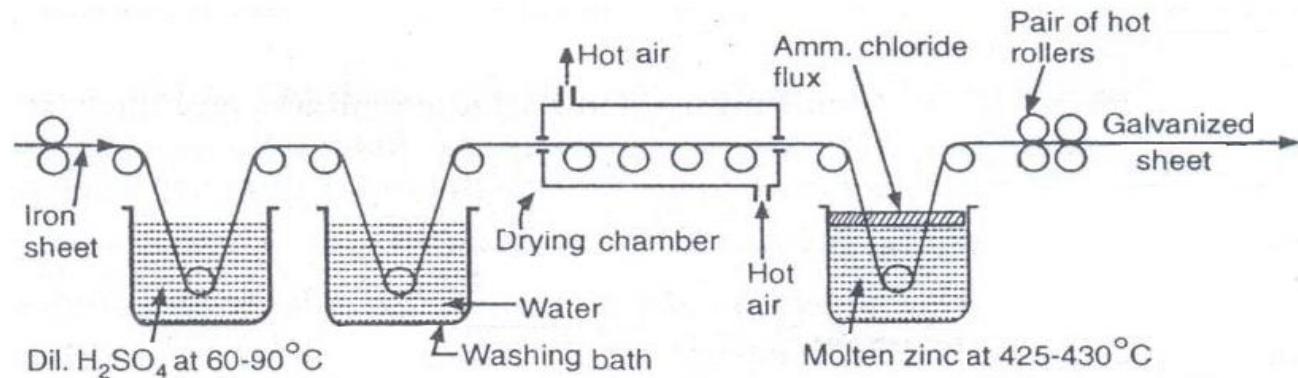
**i. Hot-dipping:** Hot dipping process is applicable to the metals having higher melting point than the coating metal. It consists of immersing well cleaned base metal in a bath containing molten coating metal, and a flux layer. The flux cleans the surface of the base metal and prevents the oxidation of the molten coating metal.

**Examples:** Coating of Zn, Sn, Pb, Al on iron, steel surfaces.

**Most widely used hot dip process are:**

- |                           |                        |
|---------------------------|------------------------|
| <b>a. Galvanizing.</b>    | <b>b. Tinning.</b>     |
| <b>c. Metal Cladding.</b> | <b>d. Cementation.</b> |

**a. Galvanizing:** Galvanizing is a process in which the iron article is protected from corrosion by coating it with a thin layer of zinc. At first iron or steel is cleaned by pickling with dilute  $H_2SO_4$  at a temperature range of  $60-90^{\circ}C$  for 15 to 20 minutes. Therefore, it removes scale, rust and other impurities present. Then after dipped molten zinc in the bath at  $425-450^{\circ}C$ , to prevent it from oxide formation, the surface of bath is covered with a flux ( $NH_4Cl$ ).

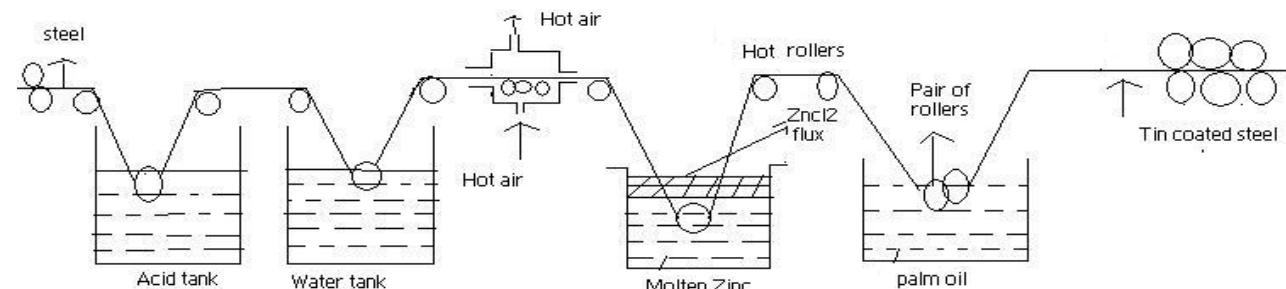


When the iron piece is taken out it is coated with a thin layer of zinc. And to remove excess zinc, it is passed through a pair of hot rollers; lastly, it is annealed at a temperature of  $450^{\circ}C$  and then cooled slowly.

### Applications of Galvanizing:

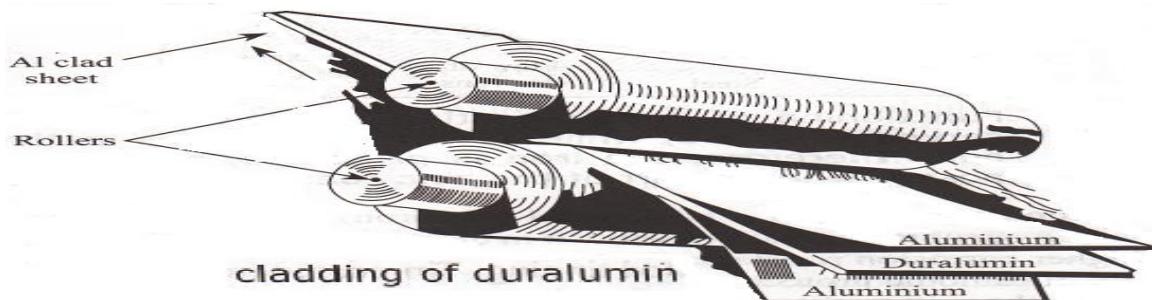
- It is widely used for protecting iron exposed to the atmosphere, as is the case with roofs, wire fences, pipes and articles fabricated from galvanized sheets like buckets, tubes.
- Galvanized ware is not used for keeping eatables because of the solubility of zinc.
- The popularity of galvanizing is due the low cost of zinc.
- Easy application and the anodic protection offered by the zinc.

**b. Tinning:** The process of coating tin over the iron or steel articles to protect it from corrosion is known as tinning. Tin is a nobler metal than iron, therefore, it is more resistance to chemical attack. In this process, at first Iron sheet is treated in dilute  $H_2SO_4$  (pickling) to remove any oxide film if present.



A cleaned Iron sheet is passed through a bath molten flux. Like Zinc chloride, then through molten tin and finally through a suitable vegetable oil. Tinning of mild steel plates is done mostly for the requirements of the food stuff industry. A cleaned iron sheet is passed through a bath of molten flux, like zinc chloride, then through molten tin and finally through a suitable vegetable oil. Lastly it is passed between rolls to adjust the thickness of the tin layer, which may be about 0.002 mm thick.

**c. Metal Cladding:** The surface to be protected is sandwiched between two thin layers of coat metal and pressed between rollers. The finished product may be welded at the edges or riveted at some points. The coat metal has to be anodic to the base metal and only plain surfaces can be cladded. This method is used for coating Al, Cr, Ni, Duralumin, etc.



a coating of a thin homogeneous layer of a coating metal on a base metal a fused so that it strongly binds permanently either on one side or on both sides and passed through rollers under heat and pressure. All corrosion-resistant metals like Ni, Cu, Ag, Au & Pt, and alloys like steel nickel alloys can be used as cladding materials. Base metals on which cladding is done are mild steel, aluminum, copper, nickel and other alloys Duralumin is very light metal alloys used in aircrafts industry.

**d. Cementation:** This type of coatings is obtained by heating the base metal in a revolving drum containing powdered coating metal. The powdered metal forms a coat on the base metal and hence protects it from corrosion.

There are three important pack cementation processes, those are: Sherardising, Chromising and Calourising.

**In Sherardising** the base metal is heated with zinc powder in a metal drum. The drum is closed and heated to 350-370 °C with slow rotation for 2-3 hours. This results in formation of **Fe-Zn alloy** on the surface of the base metal. **It is used for protecting small steel parts such as nuts, bolts, etc.**

**In chromising** the base metal is heated with a powdered mixture of 55% Chromium and 45% alumina in a metal drum. The drum is closed and heated to 1300-1400 °C with slow rotation for 2-3 hours. This results in formation of **Chrome-alloy** on the surface of the base metal. **It is used to protect gas turbine blades.**

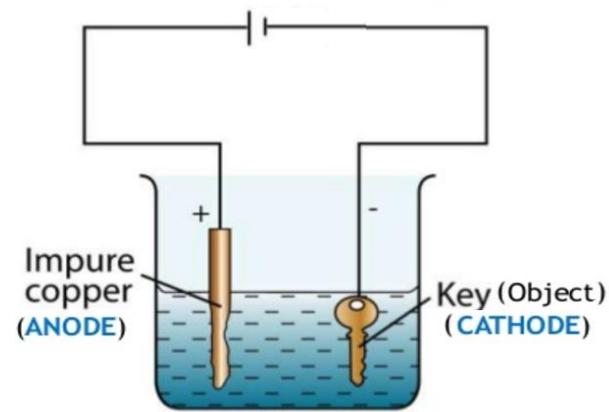
**In calorising** the base metal is heated with a powdered mixture of Aluminium and alumina in a metal drum. The drum is closed and heated to 840-950 °C with slow rotation for 4-6 hours. This results in formation of **Calorised steel**. **It is used to making of furnace parts.**

### **II. ELECTROPLATING**

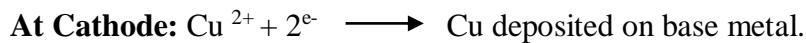
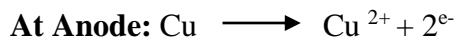
Electroplating is the process of coating metals and non-metals, to change their surface properties such as to improve the appearance, and corrosion or chemical attack. Electroplating is the electro-deposition of metal, by means electrolysis over surface of metals, alloys or non-metals.

## **Electro plating of copper over metal object:**

The metal object, to be plated is first treated with dil.HCl or dil.H<sub>2</sub>SO<sub>4</sub>. The cleaned object is made cathode of an electrolytic cell and pure copper plate as anode. CuSO<sub>4</sub> and dil.H<sub>2</sub>SO<sub>4</sub> solutions are taken as electrolyte. When the current is passed from the battery through the solution copper dissolves in the electrolyte and deposits uniformly on the metal object.



## **Chemical reactions:**



## **Conditions for Electro plating of copper over metal object:**

**Anode/coating metal:** Pure copper plate

**Cathode/Base metal:** Metal object

**Electrolyte:** CuSO<sub>4</sub> and dil.H<sub>2</sub>SO<sub>4</sub>

**Temperature:** 40-45°C

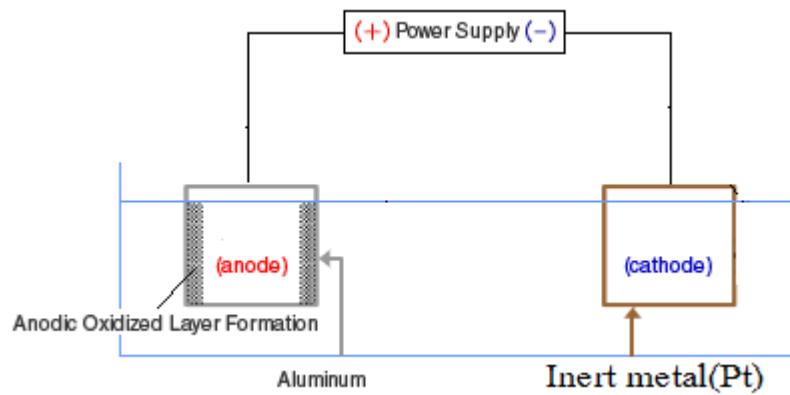
**Current:** 30-40 mA/cm<sup>2</sup>

## **Applications of electroplating are:**

- This process is widely used in automobiles, aircrafts, etc.
- Plating for decoration.
- This process is also used in Refrigerators, jewellery, radios, cameras, type-writers, umbrellas, watches etc.
- Plating on non-metallic materials.

### **III. ANODIZATION (OR) ANODIZED COATING**

**Anodization** is an electrolytic process in which a thick oxide coating is produced on the base metal. Anodised coatings are generally produced on nonferrous metals like Al, Zn, Mg and their alloys. Anodized coating on Aluminium is done by making Aluminium as an anode in an electrolytic bath containing H<sub>2</sub>SO<sub>4</sub> (or) phosphoric acid at moderate temperature about 35 to 40 °C and the cathode is a plate of lead or stainless steel. On passing the current oxidation starts at anode and oxygen combine with an anodic metal to form the oxide. The oxide film initially will be very thin and grows from the metal surface outwards and increases in thickness as oxidation continues at aluminum anode. The oxide film is very porous and soft and this can be filled by immersing it in boiling water this treatment converts porous alumina into hydrated Alumina which occupies more volume thereby the pores are sealed.



### **Chemical reactions:**

**At Anode:**  $\text{Al} + \text{O}_2 \longrightarrow \text{Al}_2\text{O}_3$  (oxide film)  
 $\text{Al}_2\text{O}_3 + \text{H}_2\text{O} \longrightarrow \text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$  (hydrated Alumina)

### **Conditions for Anodization:**

**Anode/coating metal:** Aluminium

**Electrolyte:** dil. $\text{H}_2\text{SO}_4$ ,  $\text{H}_3\text{PO}_4$

**Current:**  $0.2\text{-}2 \text{ mA/cm}^2$

**Cathode/Base metal:** Inert metal

**Temperature:**  $40\text{-}50^\circ\text{C}$

### **Advantages of Anodization:**

Very good resistance to corrosion and thicker oxide coating is more protective.

### **Applications of Anodization:**

Anodised aluminium is used in automobile engine piston.

## **IV. ELECTROLESS PLATING COATING/ ELECTROLESS NICKEL PLATING**

**Electroless plating** is a technique of depositing a noble metal (from its salt solution) on a catalytically active surface of the metal to be protected, by using a suitable reducing agent without using electrical energy.

The reducing agent reduces the metallic ions to metal, which gets plated was that catalytically activated surface giving a uniform thin coating.

Metal ions + Reducing agent  $\longrightarrow$  Metal (deposited) + oxidized products

### **IN ELECTRO LESS NICKEL PLATING HAVING THREE STEPS AS FOLLOWS:**

#### **Step I: Pretreatment and activation of the surface:**

The surface to be plated is first degreased by using organic solvents or alkali followed by acid treatment.

**Ex:**

- The surface of the stainless steel is activated by dipping in hot solution of 50% dilute sulphuric acid.
- Metals and alloys like Al, Cu, Fe, Brass, etc., can be directly nickel-plated without activation.
- Non-metallic articles like plastics, glasses are activated by dipping them in the solution containing  $\text{SnCl}_2 + \text{HCl}$ , followed by dipping in  $\text{PdCl}_2$  solution on drying a thin layer of freed is formed on the surface.

**Step II: Plating bath:** Plating bath consists of the following ingredients:

**Coating solution:**  $\text{NiCl}_2$ .

**Reducing agent:** Sodium hypophosphate.

**Complexing agent:** Sodium succinate.

**Buffer:** Sodium acetate.

**Optimum pH:** 4.5

**Optimum temperature:**  $93^\circ\text{C}$ .

**Step III: Procedure:**

The pretreated object is immersed in the plating bath for the required time. During which of the following reducing another Nickel gets coated over the object.

**Applications of Electroless-plating:**

- Electroless Ni-plating is extensively used in electronic appliances.
- Electroless Ni-plating is used domestic as well as automatic fields.
- This application is used in making jewellery.
- Electroless Ni-coated Polymers are used in decorative and functional works.
- Electroless Copper and Nickel coated plastic cabinets are used in digital as well as electronic instruments.

***Learning objectives:*****After completion of this unit the student should be able to:**

- Electrode potential, standard electrode potential.
- Types of electrodes – calomel electrode, Quinhydrone.
- Types of electrodes – glass electrode, Nernst equation.
- Determination of pH of a solution by using quinhydrone electrode.
- Determination of pH of a solution by using glass electrode.

## UNIT-III

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- Electrochemical series and its applications.
- Numerical problems, Potentiometric titrations.
- Primary batteries (Lithium cell).
- Secondary batteries (Lead–acid battery and Lithium ion battery).
- Corrosion and its control: Causes and effects of corrosion.
- Theories of chemical and electrochemical corrosion.
- Mechanism of electrochemical corrosion.
- Types of corrosion: Galvanic, water-line and pitting corrosion.
- Factors affecting rate of corrosion.
- Corrosion control methods- Cathodic protection– Sacrificial anode.
- Corrosion control methods- Impressed current cathodic methods.
- Surface coatings – metallic coatings–methods of applications.

***Short Answer Questions:***

1. Explain the Standard electrode potential with example.
2. Explain Galvanic cell?
3. What are the applications of Nernst equation?
4. What is the Construction and functioning of Calomel electrode?
5. Differentiate Primary batteries and Secondary batteries.
6. What would result when a zinc road is placed in 0.1M-ZnSO<sub>4</sub> solutions at 298 K. write the electrode reaction and calculate the potential of the electrode. Zn = - 0.7 V?
7. Write cell reaction of primary Lithium cell.
8. Define electrochemical series?
9. What is meant by rusting of Iron?
10. What is galvanic corrosion?
11. What is the effect of P<sup>H</sup> on the corrosion?
12. What is differential aeration corrosion?

## ***Descriptive Questions:***

1. Explain Construction & functioning of Glass electrode and calculate pH of unknown solution by using Glass electrode.
2. Explain Construction & functioning of Quinhydrone electrode and calculate pH of unknown solution by using Quinhydrone electrode.
3. Explain construction and functioning of Lead acid cell.
4. Describe construction and functioning of Lithium ion cell(Secondary Cell).
5. Explain the following? (a) Electroplating (b) Galvanizing (c) Tinning (d) Metal cladding.
6. Explain how corrosion control can be brought about by the following methods?  
(a) Cathodic protection (b) Sacrificial anode.

## ***Objective Questions:***

1. What is potential of Saturated Calomel electrode is. [ ]  
**a.** 0.242V                   **b.** 0.280V  
**c.** 0.333V                   **d.** 0.124V
2. A Voltaic cell converts. [ ]  
**a.** Electrical Energy in to chemical energy   **b.** Chemical energy into electrical energy  
**c.** Electrical energy into heat energy       **d.** Chemical energy into heat energy
3. Calomel is. [ ]  
**a.** Mercuric sulfate                   **b.** Mercurous sulfate  
**c.** Mercurous chloride              **d.** Mercuric chloride
4. A galvanic cell converts. [ ]  
**a.** Electrical Energy in to chemical energy   **b.** Chemical energy into electrical energy  
**c.** Electrical energy into heat energy       **d.** Chemical energy into heat energy
5. Corrosion is as an example of: [a]  
(a) Oxidation (b) Reduction           (c) Electrolysis           (d) Erosion
6. When a buried pipeline is protected from corrosion by connecting to Mg block, it is called [c]  
(a) Impressed voltage protection                   (b) Sacrificial cathodic protection  
(c) Sacrificial anodic protection                  (d) Any of these

## UNIT-III

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7. The process of coating with tin on base metal is known as: [d]  
(a) Galvanizing      (b) Zincing      (c) Sherardizing      (d) Tinning
8. The rate of corrosion of iron in atmosphere depends upon: [a]  
(a) The humidity of the atmosphere    (b) The degree of pollution of the atmosphere  
(c) The frequency of rain fall        (d) All of these factors
9. In waterline corrosion the maximum amount of corrosion takes place [c]  
(a) Along a line just above the level of the water meniscus  
(b) Along a line at the level of the water meniscus  
(c) Along a line just below the level of the water meniscus  
(d) At the bottom of the vessel

***Fill in the blanks:***

1. The Electrolyte is used in Lead-Acid storage battery is -----.
2. The net EMF of the Galvanic Cell is -----.
3. A cell whose reaction is not reversible is called -----.
4. Nernst equation for electrode reaction is -----.
5. Corrosion is a gradual decay of metal by the attack of environment.
6. The rate of corrosion increases with decrease in pH.
7. Cathodic coatings are obtained by coating a noble metal than the base metal.
8. An example of cathodic coating is tinning.
9. Impurities in metal cause corrosion.

## STEREOCHEMISTRY

Stereochemistry defines have the **same molecular formula** and sequence of bonded atoms, but **differs in the three-dimensional orientations of their atoms in space.**

**Stereoisomer's:** Compounds that have the same molecular formula and the same connectivity, but different arrangement of the atoms in 3-dimensional space. Stereoisomers cannot be converted into each other without breaking bonds.

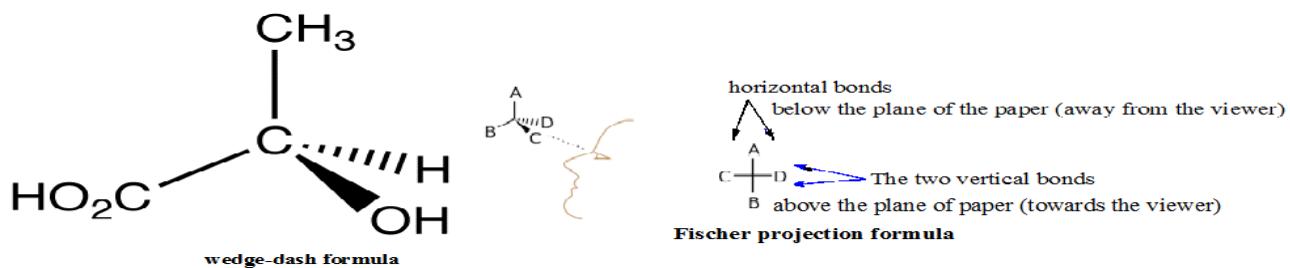
### DEFINITIONS IN STEREOCHEMISTRY

1. **Stereoisomer's:** Compounds that have the same molecular formula and the same connectivity, but different arrangement of the atoms in 3-dimensional space. Stereoisomers cannot be converted into each other without breaking bonds.
2. **Enantiomers:** Nonsuperposable mirror images (or) chiral molecules which are mirror images.
3. **Chiral (or) asymmetric carbon:** A tetrahedral carbon atom bearing four different substituents.
4. **Chirality centers (or) stereocenters:** Asymmetrically substituted atoms in a molecular structure.
5. **Diastereomers:** Stereoisomers which are not enantiomers (or mirror images).
6. **Meso compounds (or) meso forms:** Symmetric (or) achiral molecules that contain stereocenters. Meso compounds and their mirror images are not stereoisomers, since they are identical.
7. **Optical activity:** The ability of chiral substances to rotate the plane of polarized light by a specific angle.
8. **Dextrorotatory:** Ability of chiral substances to rotate the plane of polarized light to the right.
9. **Levorotatory:** Ability of chiral substances to rotate the plane of polarized light to the left.
10. **Racemic mixture (or) racemate** - A mixture consisting of equal amounts of enantiomers. A racemic mixture exhibits no optical activity because the activities of the individual enantiomers are equal and opposite in value, thereby canceling each other out.
11. **Absolute configuration** - A description of the precise 3-dimensional topography of the molecule.

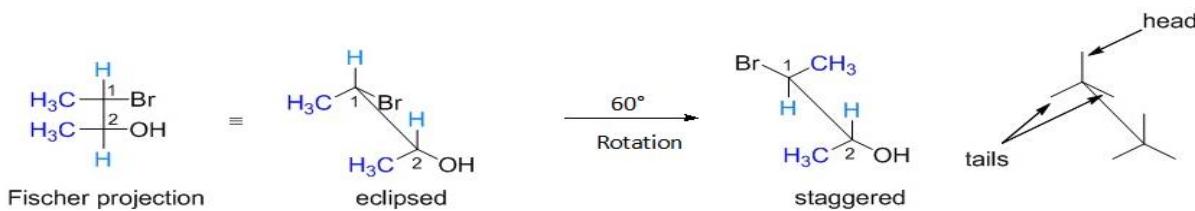
### INTRODUCTION TO REPRESENTATION OF 3-DIMENSIONAL STRUCTURES

**Fischer projection formula:** It is a representation of a 3D molecule as a flat structure where a tetrahedral carbon is represented as two crossed lines. The two vertical bonds about the stereo centre

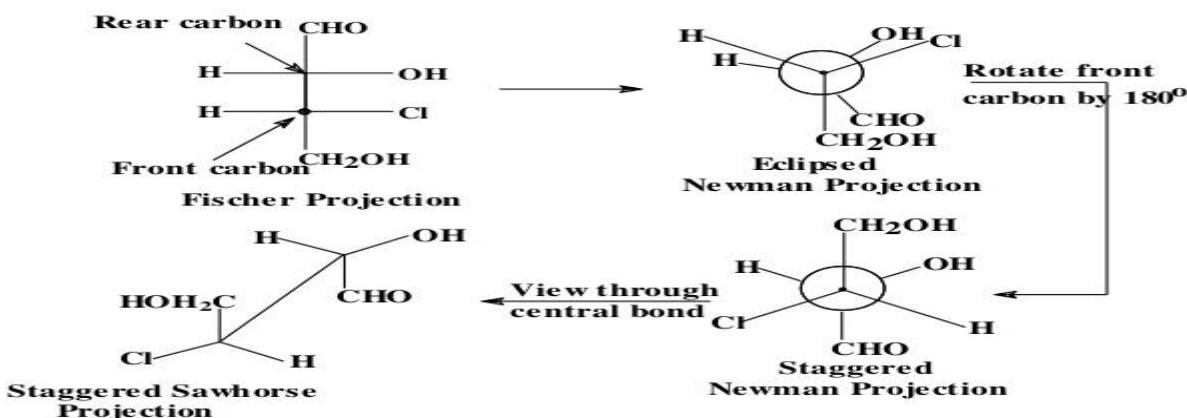
are above the plane of paper (towards the viewer) while the horizontal bonds are below the plane of the paper (away from the viewer)



**Sawhorse projection formula:** Sawhorse projection formulas are used to denote two principal stereo centers. It is a view of a molecule down a particular carbon- carbon bond, with the groups connected to both the front and back carbons are drawn using sticks at  $120^\circ$  angles. Sawhorse Projections can also be drawn so that the groups on the front carbon are staggered ( $60^\circ$  apart) or eclipsed (directly overlapping) with the groups on the back carbon. The overall representation is given below.



**Newmann projection formula:** In this notion, the molecule is again viewed by looking down a particular carbon-carbon bond. The front carbon of this bond is represented by a dot, and the back



carbon is represented by a large circle. The three remaining bonds are drawn as sticks coming off the dot (or circle), separated by one another by  $120^\circ$ . Just like Sawhorse projection formula, Newman

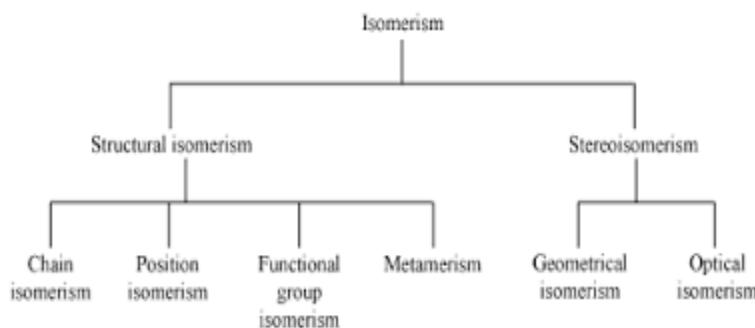
# UNIT-IV

Projection can be drawn such that the groups on the front carbon are staggered ( $60^\circ$  apart) or eclipsed (directly overlapping) with the groups on the back carbon.

## CLASSIFICATION OF STRUCTURAL AND STEREOISOMER'S

Compounds which have same molecular formula but differ in arrangement of atoms within the molecule are known as **isomers** and this phenomenon is known as isomerism. Isomers can have different physical or chemical properties.

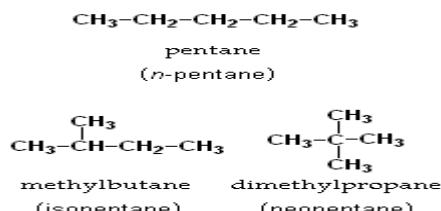
**Classification of isomerism:** There are two main types of isomerism- structural isomerism and stereoisomerism. These can be further classified as:



**I. Structural Isomerism:** Structural isomerism, or constitutional isomerism, is a type of isomerism where isomers have same molecular formula but have different arrangements of atoms within the molecule. Structural isomerism can be further classified as:

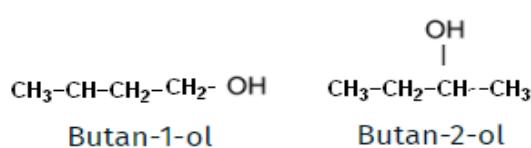
### 1. Chain isomerism:

Formula but they differ in the order in which the carbon atoms are bonded to each other.



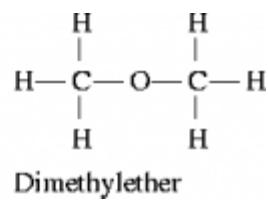
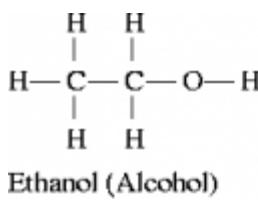
### 2. Position isomerism:

Position isomerism is a type of structural isomerism where the main carbon skeletons are same but they differ in the position of functional group attached to it.



### 3. Functional group isomerism:

Functional group isomerism is a type of structural isomerism where isomers have same molecular formula but differ in functional group.



### 4. Tautomerism:

Tautomerism is a special type of structural isomerism where the isomer stays in dynamic equilibrium with each other by simple proton transfer in an intramolecular fashion.



## II. Stereoisomerism:

Stereoisomer's are isomers that have same molecular formula, same sequence of bonding of atoms but differ in their three dimensional orientation of atoms in space. Stereoisomerisms are of two types:

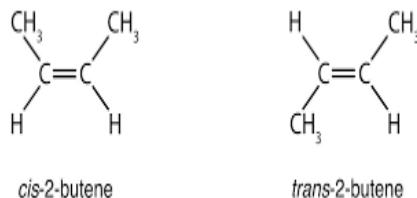
1. Geometrical isomerism
2. Optical isomerism

**1. Geometrical isomerism:** Geometrical isomers are molecules that are locked into their spatial positions with respect to one another due to a double bond.

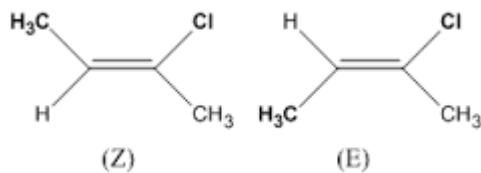
Geometric isomers differ from one another in physical properties like melting and boiling points.

Geometrical isomers are two types that are *Cis-trans* isomerism

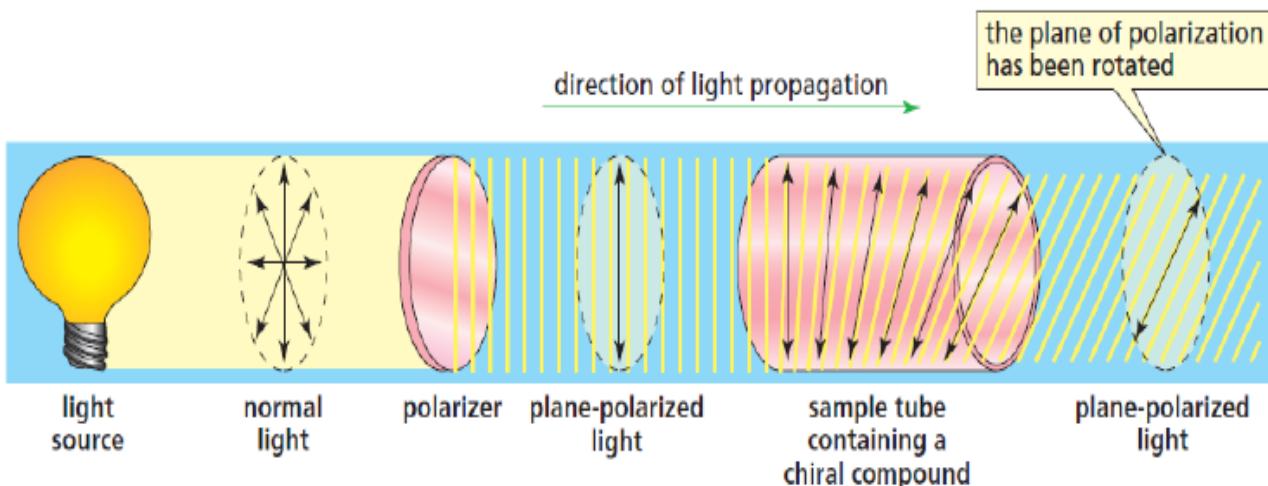
- Cis indicates that the functional groups are on the same side of the carbon chain.
- Trans conveys that functional groups are on opposing sides of the carbon chain.



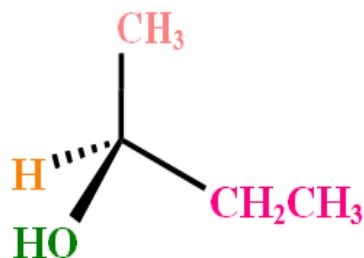
- It is not to be confused with E-Z isomerism, which is an absolute stereochemical description, and only to be used with alkenes. In general, stereoisomers contain double bonds that do not rotate, or they may contain ring structures, where the rotation of bonds is restricted or prevented.



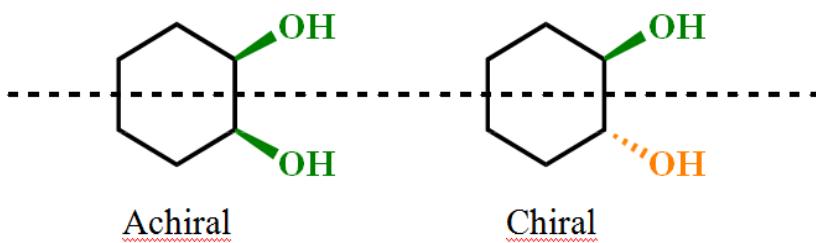
**2. Optical isomerism:** Compounds which have similar chemical and physical properties and differ only in their optical activity are known as optical isomers and phenomenon as optical isomerism.



- Certain substances have a remarkable power of rotating the plane polarized light (PPL) either towards left (or) towards right.
- The isomer which rotates the plane polarized light to left is known as laevo (l).
- The isomer which rotates the plane polarized light to right is known as dextro (d).
- The phenomenon of rotating the plane polarized light is known as optical activity and compounds exhibiting this property are known as **optically active** compounds.
- A carbon atom bonded to four different groups could lead to optical activity and is called a stereogenic center.
- **Ex:** 2-Butanol:



- In general organic compounds, which lack a plane of symmetry are optical active and are called **chiral** compounds.



**ENANTIOMERS**

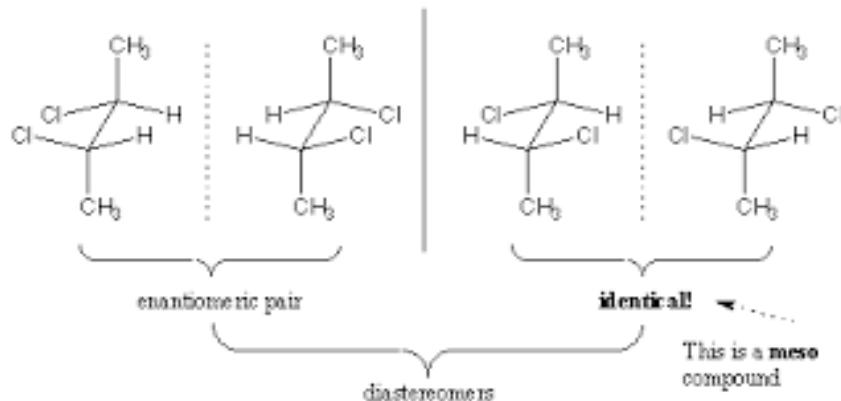
- Optical isomers that are mirror images are called Enantiomers.
- These always exist as discrete pairs.
- Enantiomers are stable, isolable compounds that differ from one another in three-dimensional spatial arrangements.
- Enantiomers have identical properties in all respects except in their interaction with plane of polarized light.
- Enantiomers have the same melting point, density, solubility, color and reactivity toward acids and bases.



- They differ, however, in the direction in which they rotate the plane polarized light.
- Both rotate the plane of polarized light to exactly the same extent (same angle) but one rotates the plane to the right (clockwise: called dextrorotatory). While the other rotates the plane to the left (anticlockwise: called levorotatory).

**DIASTEREOMERS**

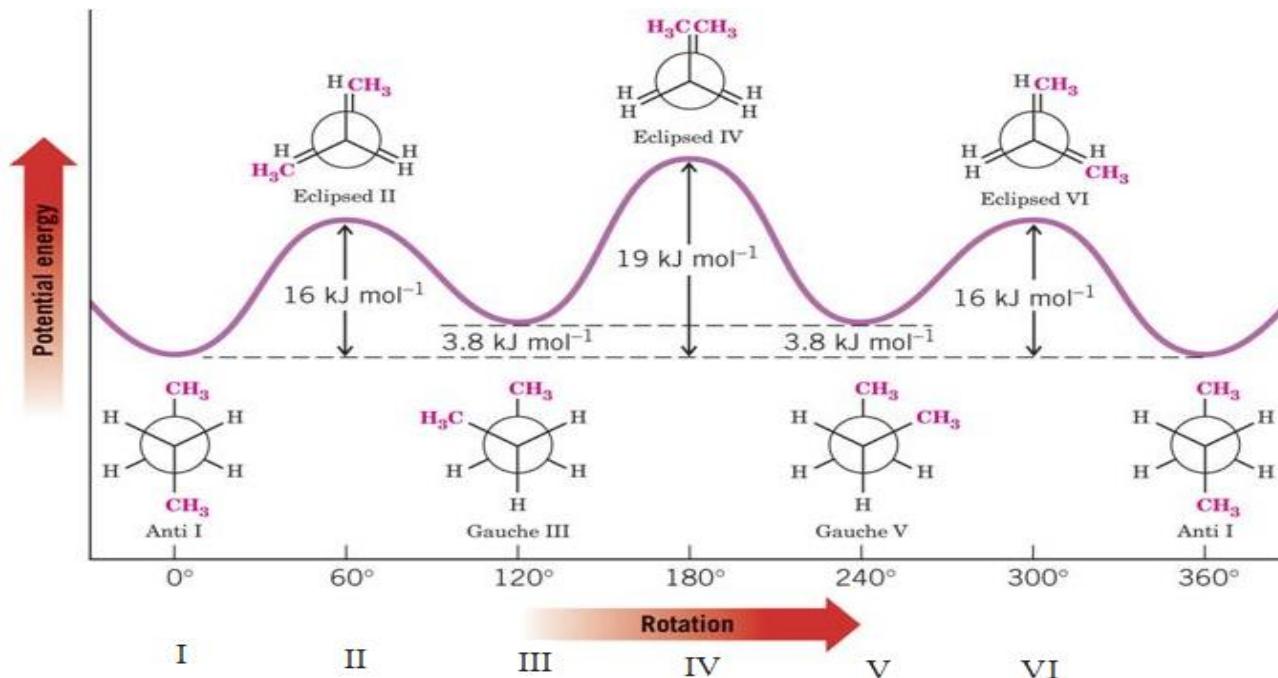
- Optical isomers that are not mirror images of each other and non-superimposable.
- Diastereomers can have different physical properties and reactivity.
- They have different melting points and boiling points and different densities.
- They have two or more stereocenters.



## CONFORMATION ANALYSIS OF n-BUTANE

The molecular formula of n-Butane is  $\text{CH}_3\text{CH}_2\text{-CH}_2\text{-CH}_3$ , in this there are now three rotating carbon-carbon bonds to consider, but we will focus on the middle bond between  $\text{C}_2$  and  $\text{C}_3$ . Below are two representations of butane in a conformation which puts the two  $\text{CH}_3$  groups ( $\text{C}_1$  and  $\text{C}_4$ ) in the eclipsed position.

DIHEDRAL ANGLE	CONFORMATION OF BUTANE	ENERGY(kJ/mol)
Butane - $0^\circ$	Staggered	0
Butane - $60^\circ$	Partial Eclipsed	16
Butane - $120^\circ$	Gauche	3.8
Butane - $180^\circ$	Fully Eclipsed	19
Butane - $240^\circ$	Gauche	3.8
Butane - $300^\circ$	Partial Eclipsed	16
Butane - $360^\circ$	Staggered	0



**Stability Order:** I > III & V > II & VI > IV

- III and V conformations of Butane are enantiomers.
- I and III conformations of Butane are diastereomers.
- I and V conformations of Butane are diastereomers.

**ABSOLUTE CONFIGURATION**

There are three steps to assign **R or S**, which is called the absolute configuration of the chiral carbon atom. Groups are first assigned a priority based on the atomic weight of the first atom bonded to the chiral carbon, which can be found on a periodic table. The higher the atomic weight, the higher priority.

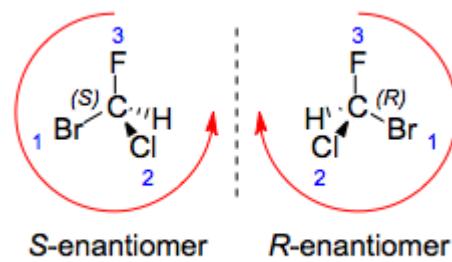
**Rules for the absolute configuration:**

1. Point the lowest priority group away from you. This means that the low priority group needs be on the dashed wedge in the example below.
2. Number the remaining three groups according to priority: 1 = highest priority and 3 = lowest priority.
3. Draw a circle beginning at the group numbered 1 that ends with an arrow at group 3.

If the arrow points **clockwise**, the compound is **R**. If the arrow points in a **counterclockwise direction**, the chiral carbon is **S**.

**Assigning Chirality When the Group Contains Multiple Atoms:**

When the groups contain more than one atom, we may need to look beyond the first atom to assign the absolute configuration. The example on the left is fairly straightforward. The first group is CH<sub>2</sub> in two chains, so we need to look beyond that position. As we move outward one atom, we can see that the nitrogen has higher priority than another carbon atom, which makes this compound **R**. In the example on the right, the groups contain only carbon and hydrogen, but they are different groups:



**REACTION MECHANISMS**

The chemical reactions happening between electron donors and acceptors are described by concepts like **electrophile** and **nucleophile**. These are the most important concepts in organic chemistry.

**Electrophile:**

The term electrophile can be split into “electro-electron” and “phile-loving”.

- They are electron deficient and hence electrons loving.
- They are positively charged or neutrally charged, they attract electrons.
- Movement of electrons depends on the density. They move from high density area to low density area.
- They undergo electrophilic addition and electrophilic substitution reactions.
- Electrophile is also called as Lewis acid.

**Nucleophile:**

The term nucleophile can be split into “nucleo-nucleus” and “phile-loving”.

- They are electron rich and hence nucleus loving.
- They are negatively charged or neutrally charged, they donate electrons.
- Movement of electrons depends on the density. They move from low density area to high density area.
- They undergo nucleophilic addition and nucleophilic substitution reactions.
- Nucleophile is also called as Lewis base.

**DIFFERENCES BETWEEN ELECTROPHILES AND NUCLEOPHILES**

ELECTROPHILE	NUCLEOPHILE
Electron deficient	Electron rich
They are positively charged / neutral	They are negatively charged / neutral
Also called as Lewis acid	Also called as Lewis base
They undergo electrophilic addition and electrophilic substitution reactions.	They undergo nucleophilic addition and nucleophilic substitution reactions.
It accepts pair of electron to form covalent bond	It donates pair of electron to form covalent bond
All carbocations	All carboanions
<b>Example:</b> Hydronium ion, $\text{Cl}^+$ , $\text{NO}_2^+$ , $\text{BF}_3$ , $\text{CH}_3^+$	<b>Example:</b> Chloride ion, $\text{C}_2\text{H}_5\text{O}^-$ , $\text{HS}^-$ , $\text{H}_2\text{N}^-$ , $(\text{CH}_3)_3\text{N}^-$

# UNIT-IV

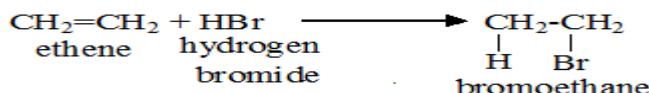
<b>DIFFERENCES BETWEEN CARBOCATION AND CARBANION</b>	
<b>Carbocation</b>	<b>Carbanion</b>
It is an electron deficient species.	It is an electron rich species.
The carbon involved is $Sp^2$ hybridized.	The carbon involved is $Sp^3$ hybridized.
It has a planar geometry.	It has a tetrahedral geometry.
It is lewis acid.	It is lewis base.
It is electrophile.	It is nucleophile.
It accepts pair of electron to form covalent bond.	It donates pair of electron to form covalent bond.
Stability order of Carbocations:	Stability order of Carbanions:
$\begin{array}{c} \oplus \\ CH_3 \end{array}$ $\begin{array}{c} \oplus \\ CH_3CH_2 \end{array}$ $\begin{array}{c} \oplus \\ CH_3CCH_3 \end{array}$ $\begin{array}{c} CH_3 \\   \\ H_3C-C\oplus \\   \\ CH_3 \end{array}$ 	$\begin{array}{c} \ominus \\ CH_3 \end{array}$ $\begin{array}{c} \ominus \\ CH_3CH_2 \end{array}$ $\begin{array}{c} \ominus \\ CH_3CHCH_3 \end{array}$ $\begin{array}{c} CH_3 \\   \\ H_3C-\overset{\ominus}{C} \\   \\ CH_3 \end{array}$ 
<b>Example:</b> Hydronium ion, $Cl^+$ , $NO_2^+$ , $BF_3$ , $CH_3^+$	<b>Example:</b> Chloride ion, $C_2H_5O^-$ , $HS^-$ , $H_2N^-$ , $(CH_3)_3N^-$

## ADDITION REACTIONS

These reactions are given by those compounds which have at least one  $\pi$  bond ( $>C=C<$ ,  $-C\equiv C-$ ).

In addition reaction there is loss of one  $\pi$  bond and gain of two  $\sigma$  bonds. Thus product of the reaction is generally more stable than the reactant. The reaction is a spontaneous reaction.

**Ex:** when hydrogen bromide reacts with ethene we, get bromoethane



### Types of addition reactions:

Addition reactions can be classified into three categories on the basis of the nature of initiating species. **i.** Electrophilic additions **ii.** Nucleophilic additions **iii.** Free radical additions

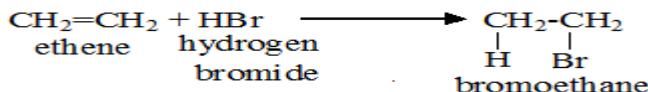
#### **i. ELECTROPHILIC ADDITION REACTIONS:**

- Electrophilic addition reactions are mainly given by alkenes and alkynes.
- Electrophilic addition reactions of alkenes and alkynes are generally two step reactions.
- Alkenes and alkynes give electrophilic addition with those reagents which on dissociation gives electrophile as well as nucleophile.

## UNIT-IV

- If the reagent is a weak acid then electrophilic addition is catalysed by strong acids (Generally H<sub>2</sub>SO<sub>4</sub>).

**Ex:** when hydrogen bromide reacts with ethene we, get bromoethane

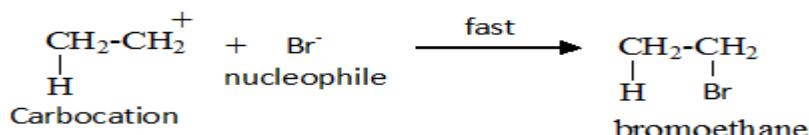


**Mechanism of Electrophile addition: Ethene to hydrogen bromide:**

**Step-1:** Attack by the electrophile opening the double bond and producing an intermediate **Carbocation** and leaving a negative bromide ion.



**Step-2:** The intermediate, carbocation reacts with nucleophile and produce product, bromoethane.



### **MARKOWNIKOFFS RULE:**

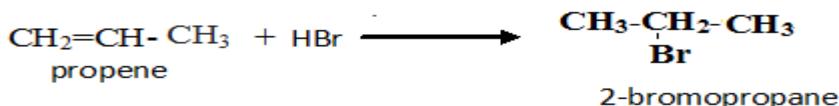
The negative part of the addendum adds on that doubly bonded carbon of the alkene which has least number of hydrogen atoms.

This rule can be used only in those alkenes which fulfill the following conditions:

- Alkene should be unsymmetrical.
- Substituent/substituents present on doubly bonded carbon(s) should only be +I group.

### **Example: Addition of HBr to propene:**

According to this rule, the product formed is 2-bromopropane as the major product.



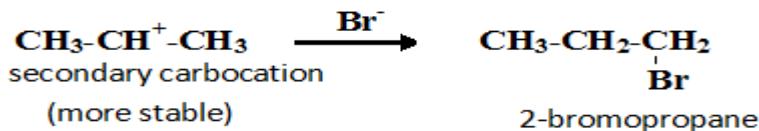
### **Mechanism of Markownikoff's rule:**

The secondary carbocation obtained in the below mechanism is more stable than the primary carbocation, therefore the product of secondary carbocation predominates because it is formed at a faster rate.

UNIT-IV



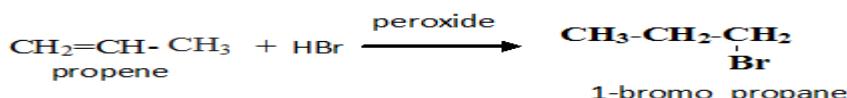
The secondary carbocation is attacked by  $\text{Br}^-$  ion to form 2-bromopropane as the major product.



### **Anti Markownikoff's rule:**

If negative part of the addendum gets attached to that carbon atom which possesses higher number of hydrogen atoms.

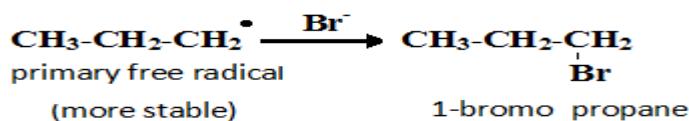
**Example: Addition of HBr to propene:** In the presence of peroxide, addition of HBr to propene takes place opposite to the Markovnikoff rule.



**Mechanism of Anti Markownikoff's rule:** The primary free radical obtained in the below mechanism is more stable than the secondary free radical.



This explains the formation of 1-bromopropane as the major product.

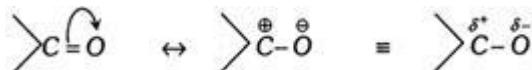


## ii. NUCLEOPHILIC ADDITION REACTIONS:

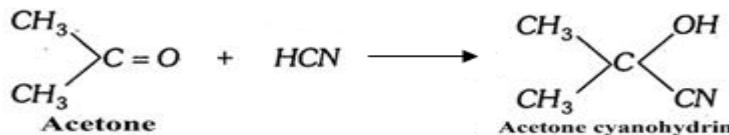
- When the addition reaction occurs on account of the initial attack of nucleophile, the reaction is said to be a nucleophilic addition reaction.
  - Due to presence of strongly electronegative oxygen atom, the  $\pi$ -electrons of the carbon-oxygen double bond in carbonyl group ( $C=O$ ) get shifted towards the oxygen atom and thereby such bond is highly polarised.

## UNIT-IV

- This makes carbon atom of the carbonyl group electron deficient.



**Example:** The addition of HCN to acetone is an example of nucleophilic addition.

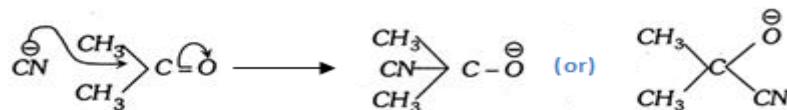


**The mechanism of the reaction involves the following steps:**

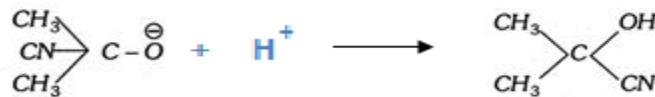
**Step1:** HCN gives a proton ( $\text{H}^{\oplus}$ ) and a nucleophile, cyanide ion ( $\text{CN}^{\ominus}$ )



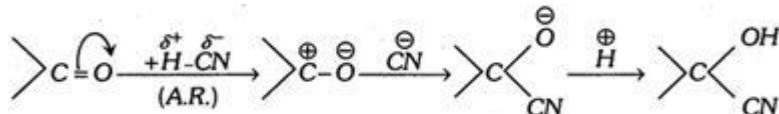
**Step2:** The nucleophile ( $\text{CN}^{\ominus}$ ) attacks the positively charged carbon so as to form an anion ( $\text{H}^{\oplus}$  does not initiate the negatively charged oxygen as anion is more stable than cation).



**Step3:** The proton ( $\text{H}^{\oplus}$ ) combines with anion to form the addition product.



In  $\text{C}=\text{O}$  compounds, the addition of liquid HCN gives cyanohydrin and the addendum is  $\text{CN}^-$  ion and not HCN directly (addition is catalysed by bases or salts of weak acids and retarded by acids or unaffected by neutral compounds).



### **GRIGNARD ADDITION OF CARBONYL COMPOUNDS**

When an alkyl halide reacts with Magnesium metal in presence of dry ether, the compound formed is Alkyl Magnesium halide, which is also known as Grignard reagent.



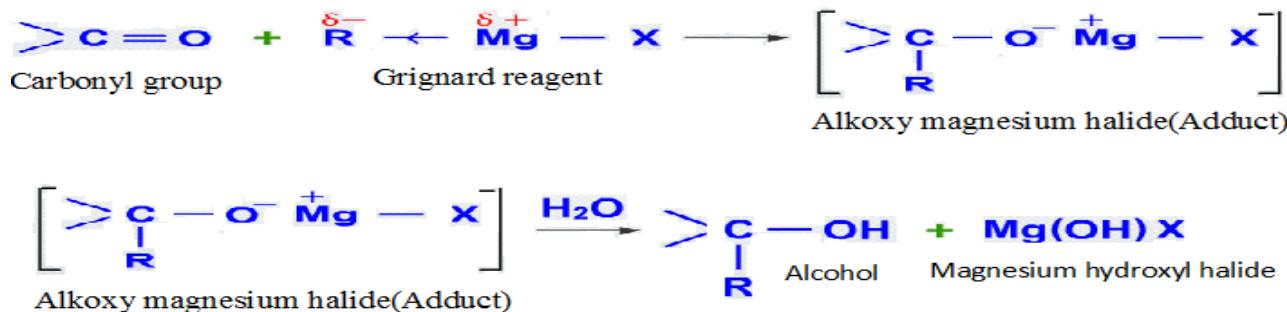
The Grignard reagent is represented as **R-Mg-X**, where **R** = alkyl / aryl / alkenyl / allyl group  
**X** = Cl / Br / I

## UNIT-IV

**Note:** Grignard reagent is highly polar compound. It is also known as Organometallic compound. When Grignard reagent reacts with such type of compounds, having active hydrogen atom, hydrocarbons are formed.

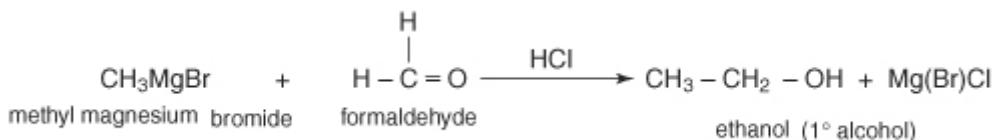


### THE MECHANISM OF GRIGNARD ADDITION OF CARBONYL COMPOUNDS:



**Grignard addition of carbonyl compounds:** The Grignard reaction is the only simple method available that is capable of producing primary, secondary, and tertiary alcohols.

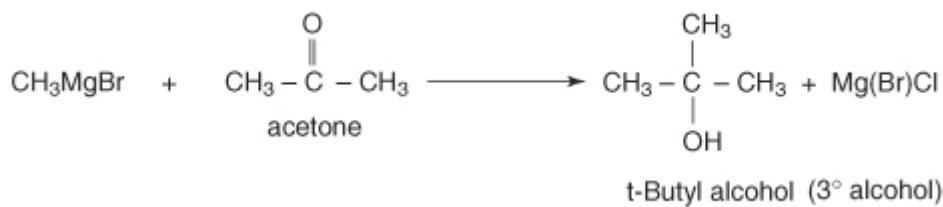
- i. To produce a primary alcohol, the Grignard reagent is reacted with **formaldehyde**.



- ii. Reacting a Grignard reagent with **any other aldehyde (acetaldehyde)** will lead to a secondary alcohol.



- iii. Reacting a Grignard reagent with a **ketone (acetone)** will generate a tertiary alcohol.



**SUBSTITUTION REACTIONS**

A reaction in which the functional group of one chemical compound is substituted by another group  
(or)

It is a reaction which involves the replacement of one atom or a molecule of a compound with another atom or molecule.

**Ex:** The reaction of Ethanol with the hydrogen iodide which forms iodoethane along with water.

**Conditions for Substitution Reaction:**

- The strong base such as NaOH has to be in dilute form. Suppose if the base is of higher concentration, there are chances of dehydrohalogenation taking place.
- Maintaining low temperatures such as room temperature.
- The solution needs to be in an aqueous state such as water

**Types of Substitution Reactions:** Substitution Reactions are of two types

i. Electrophilic reactions ii. Nucleophilic reaction

These two types of reactions mainly differ in the kind of atom which is attached to its original molecule. In the nucleophilic reactions the atom is said to be electron-rich species, whereas, in the electrophilic reaction, the atom is an electron-deficient species.

i. **Electrophilic substitution reactions:** The electrophilic substitution reaction involves the electrophiles. Electrophiles are those which donate a pair of electrons in the formation of a covalent bond. The Electrophilic reactions occur mostly with the aromatic compounds. These compounds have about an excess of electrons that can be shared throughout the system of reaction.

The Electrophilic substitution reactions are basically defined as those chemical reactions where the electrophile replaces the functional group in a compound but not the hydrogen atom.

**Example:** The species of electrophiles include hydronium ion ( $\text{H}_3\text{O}^+$ ), halides of hydrogen such as HCl, HBr, HI, sulfur trioxide ( $\text{SO}_3$ ), the nitronium ion ( $\text{NO}_2^+$ ), etc.

**NUCLEOPHILIC SUBSTITUTION REACTIONS**

The nucleophilic substitution reaction involves the nucleophiles. These are said to be fully charged (or) have negative ions present on a molecule. The common **examples** of nucleophiles are cyanide ions, water, hydroxide ions, and ammonia. In Nucleophilic substitution reaction, where a nucleophile gets attached to the positive charged atoms or molecules of the other substance.

**Example:** The hydrolysis of alkyl bromide ( $\text{R}-\text{Br}$ ), under the basic conditions, where in the nucleophile is nothing but the base  $\text{OH}^-$ , whereas the leaving group is the  $\text{Br}^-$ . The reaction for the following is as given below

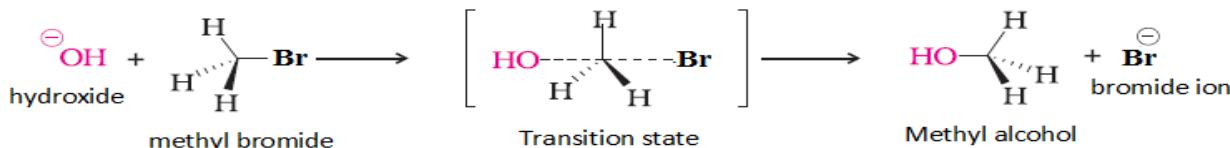


**The  $\text{S}_{\text{N}}2$  (Bi molecular nucleophilic substitution reaction) Reaction Mechanism:**

The reaction between methyl bromide and hydroxide ion to yield methanol follows second order kinetics; that is, the rate depends upon the concentrations of both reactants:



The simplest way to account for the kinetics is to assume that reaction requires a collision between a hydroxide ion and a methyl bromide molecule. In its attack, the hydroxide ion stays far away as possible from the bromine; i.e. it attacks the molecule from the rear and begins to overlap with the tail of the  $\text{sp}^3$  hybrid orbital holding ‘Br’. The reaction is believed to take place as shown:



In the **Transition state** the carbon is partially bonded to both -OH and - Br; the C-OH bond is not completely formed, the C- Br bond is not yet completely broken. Hydroxide has a diminished -ve charge, since it has begun to share its electrons with carbon. Bromine has developed a partial negative charge, since it has partially removed a pair of electrons from carbon. At the same time, of course, ion dipole bonds between hydroxide ion and solvent are being broken and ion-dipole bonds between bromide ion and solvent are being formed.

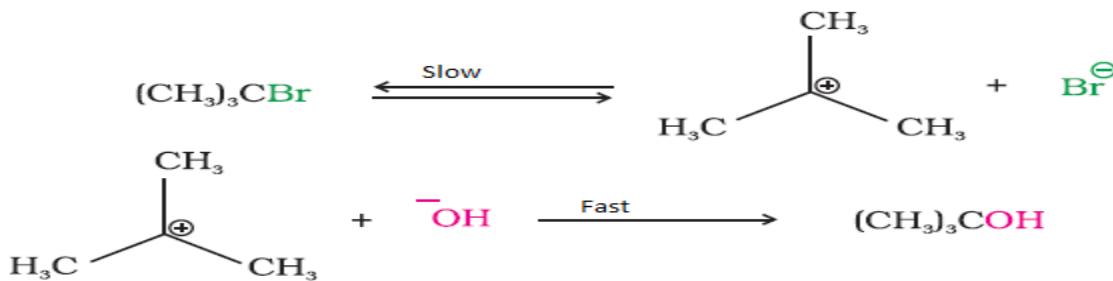
As the -OH becomes attached to C, 3 bonds are forced apart ( $120^\circ$ ) until they reach the spoke arrangement of the **Transition state**; then as bromide is expelled, they move on to the tetrahedral arrangement opposite to the original one. The process has often been likened to the turning inside out of an umbrella in a gale.

**Reactivity:** In  $\text{S}_{\text{N}}2$  reactions the order of reactivity of RX is  $\text{CH}_3\text{X} > 1^\circ > 2^\circ > 3^\circ$ .

Differences in rate between two  $\text{S}_{\text{N}}2$  reactions seem to be chiefly due to **steric factors** (bulk of the substituents) and not due to electronic factors i.e. ability to withdraw or release electrons.

**The S<sub>N</sub>1 (Uni molecular nucliophilic substitution reaction) Reaction Mechanism:**

The reaction between tert-butyl bromide and hydroxide ion to yield tert-butyl alcohol follows first order kinetics; i.e., the rate depends upon the concentration of only one reactant, tert-butyl bromide.

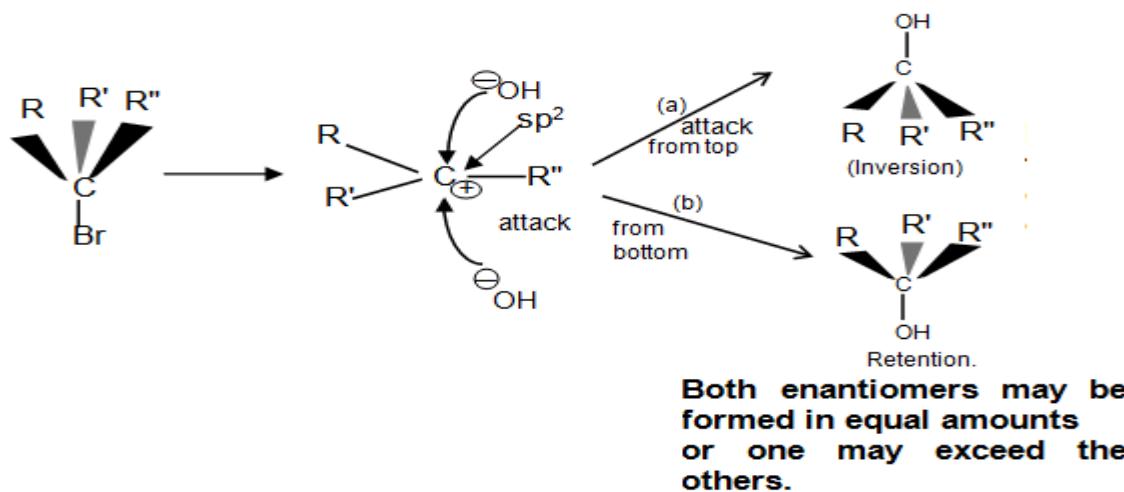


Rate = K[Br] S<sub>N</sub>1 reaction K follows first order kinetics.

The optically active bromide ionizes to form bromide ion and the **flat carbocation**. The nucleophilic reagent then attaches itself to carbonium ion from either face of the flat ion.

If the attacks were purely random, we would expect equal amounts of two isomers; i.e. we would expect only the racemic modification. But the product is not completely racemized, for the inverted product exceeds its enantiomer.

We can say in contrast to S<sub>N</sub>2 reaction, which proceeds with complete inversion; **an S<sub>N</sub>1 reaction proceeds with racemization though may not be complete.**

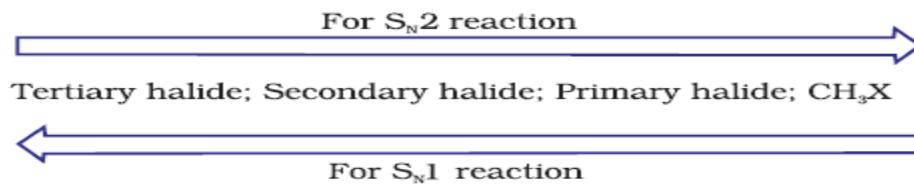


Reactivity of an alkyl halide depends chiefly upon how stable a carbonium ion it can form.

In S<sub>N</sub>1 reactions the order of reactivity of alkyl halides is **Allyl, benzyl > 3° > 2° > 1° > CH<sub>3</sub> X.** 3° alkyl halides undergo S<sub>N</sub>1 reaction very fast because of the high stability of 3° carbocations.

# UNIT-IV

**Order of reactivity of alkyl halides towards S<sub>N</sub>1 and S<sub>N</sub>2 reactions as follows:**



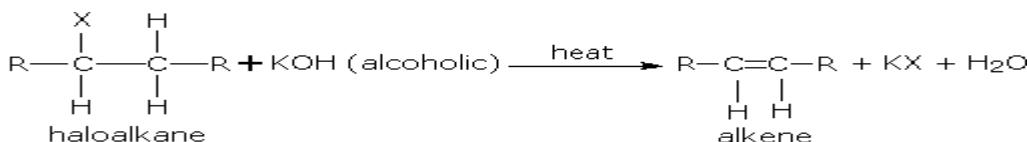
**Differences between S<sub>N</sub>1 and S<sub>N</sub>2:**

	S <sub>N</sub> 1 <b>(Uni molecular nucliophilic substitution reaction)</b>	S <sub>N</sub> 2 <b>(Bi molecular nucliophilic substitution reaction)</b>
<b>Steps</b>	Two : <b>1:</b> R:X → R <sup>+</sup> + X <sup>-</sup> <b>2:</b> R <sup>+</sup> + Nu <sup>-</sup> → RNu	One : R:X + Nu <sup>-</sup> → RNu + X <sup>-</sup>
<b>Rate</b>	=K [RX] (1st order)	=K[RX] [:Nu <sup>-</sup> ] (2nd order)
<b>Transition State of slow step</b>		
<b>Stereochemistry</b>	Inversion and racemization (Top and bottom attack)	Inversion (backside attack)
<b>Molecularity</b>	Unimolecular	Bimolecular
<b>Reactivity of 'R'</b> <b>Determining Factor</b>	3° > 2° > 1° > CH <sub>3</sub> (Stability of R <sup>+</sup> )	CH <sub>3</sub> > 1° > 2° > 3° (Steric hindrance in R group)
<b>Nature of 'X'</b>	RI > RBr > RCl > RF	RI > RBr > RCl > RF with Nu <sup>-</sup>
<b>Solvent effect on rate</b>	Rate increases in polar solvent	Rate increase in polar aprotic solvents.
<b>Effect of nucleophile</b>	No effect as it does not appear in the rate expression.	Rate depends on nucleophilicity I <sup>-</sup> > Br <sup>-</sup> > Cl <sup>-</sup> ; RS <sup>-</sup> > RO <sup>-</sup>
<b>Catalysis</b>	Lewis acid, eg. Ag <sup>+</sup> , AlCl <sub>3</sub> , ZnCl <sub>2</sub>	None
<b>Competitive reaction</b>	Elimination, rearrangement	Elimination

**ELIMINATION REACTIONS**

Elimination reactions are commonly known by the kind of atoms or groups of atoms leaving the molecule.

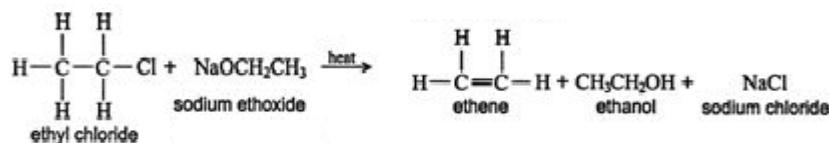
- The removal of a hydrogen atom and a halogen atom is known as **dehydrohalogenation**.
- When both leaving atoms are halogens, the reaction is known as **dehalogenation**.
- The elimination of a water molecule, usually from an alcohol, is known as **dehydration**.
- When both leaving atoms are hydrogen atoms, the reaction is known as **dehydrogenation**.



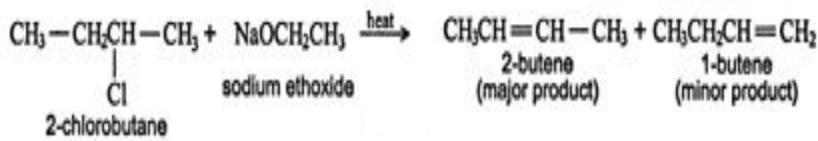
It is the principal process by which organic compounds containing only single carbon-carbon bonds (saturated compounds) are transformed to compounds containing double or triple carbon-carbon bonds (unsaturated compounds).

**DEHYDROHALOGENATION OF ALKYL HALIDES:**

The dehydrohalogenation of alkyl halides, another  $\beta$  elimination reaction, involves the loss of a hydrogen and a halide from an alkyl halide ( $RX$ ). Dehydrohalogenation is normally accomplished by reacting the alkyl halide with a strong base, such as sodium ethoxide.

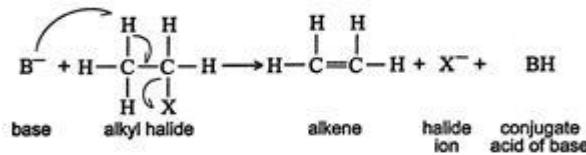


This reaction also follows the Saytzeff rule, so in the reaction of 2-chlorobutane with sodium ethoxide, the major product is 2-butene.



**MECHANISM:**

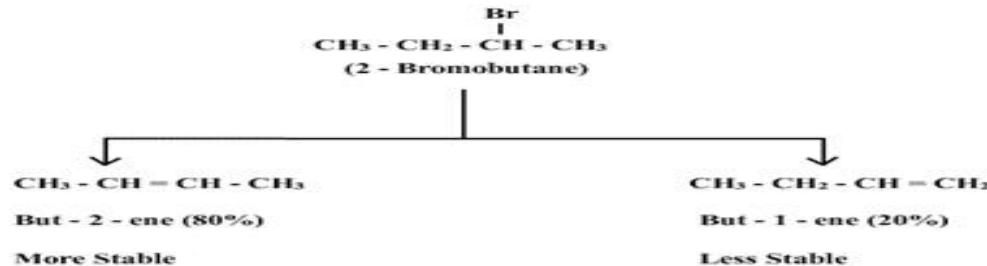
- A strong base removes a slightly acidic hydrogen proton from the alkyl halide via an acid-base reaction.
- The electrons from the broken hydrogen-carbon bond are attracted toward the slightly positive carbon atom attached to the chlorine atom. As these electrons approach the second carbon, the halogen atom breaks free, leading to the formation of the double bond.



The order of reactivity of haloalkanes in dehydrohalogenation is, Tertiary > Secondary > Primary.

### **SAYTZEFF'S RULE / ZAITSEV'S RULE**

According to Saytzeff rule "In dehydrohalogenation reactions, the preferred product is that alkene which has the greater number of alkyl groups attached to the doubly bonded carbon atoms." For example: The dehydrohalogenation of 2-bromobutane yields two products 1-butene and 2-butene. Out of these 2-butene is the major product (80%) as it is more highly substituted and it is more stable.

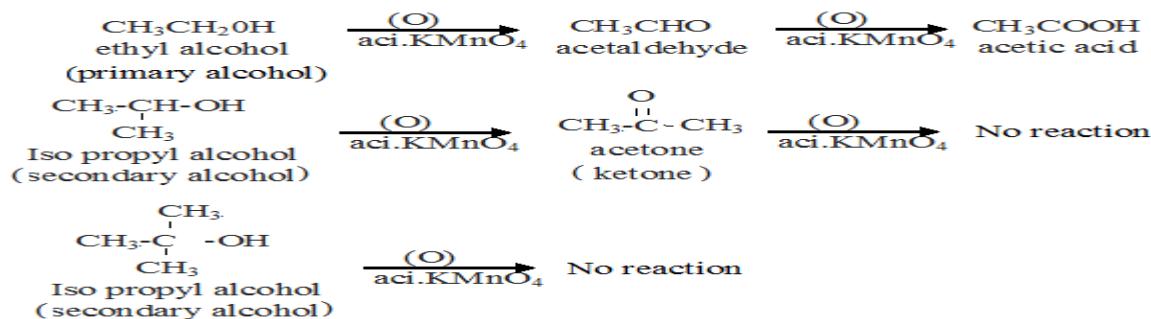


### **OXIDATION REACTIONS**

#### **Oxidation of alcohols by using of Potassium permanganate (KMnO<sub>4</sub>):**

Potassium permanganate is a very strong oxidizing agent and able to react with many functional groups especially secondary alcohols. Under controlled conditions KMnO<sub>4</sub> oxidizes primary alcohols to Carboxylic acids very efficiently.

**Example:** Acidified KMnO<sub>4</sub> oxidizes the ethyl alcohol (primary alcohol) directly to the carboxylic acid. Acidified KMnO<sub>4</sub> oxidizes the Iso propyl alcohol (secondary alcohol) to ketone and no further

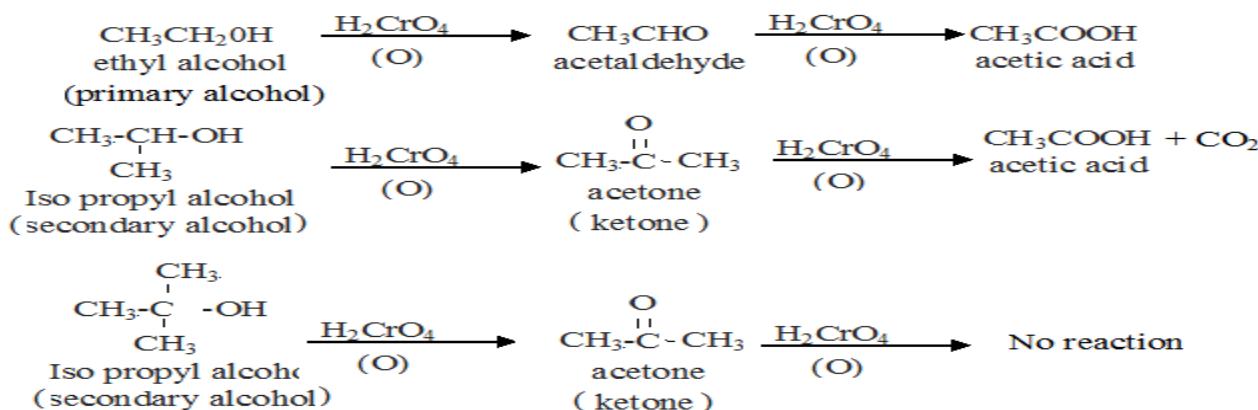


reaction. There is no reaction with Acidified KMnO<sub>4</sub> to tertiary alcohols.

**Oxidation of alcohols by using of Chromic acid ( $H_2CrO_4$ ):**

Chromic acid strong acid and it is a reagent for oxidizing alcohols to ketones and carboxylic acids.

**Example:** Generally Chromic acid oxidizes primary alcohols (ethyl alcohol) to carboxylic acids (acetic acid), secondary alcohols (iso propyl alcohol) to ketones (acetone), Carbon dioxide and finally carboxylic acids (acetic acid). Chromic acid oxidizes the tertiary alcohol (secondary alcohol) to ketone and no further reaction.



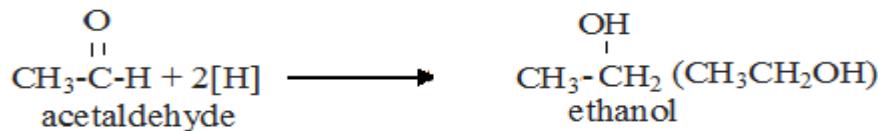
**REDUCTION REACTIONS OF CARBONYL COMPOUNDS BY USING  $\text{LiAlH}_4$  &  $\text{NaBH}_4$**

Metal hydrides like lithium aluminium hydride ( $\text{LiAlH}_4$ ), sodium borohydride ( $\text{NaBH}_4$ ) reduce carbonyl compounds to alcohols. These are hydride ion ( $\text{H}^-$ ) donors. Hydride ion is a nucleophile, hence it is a nucleophilic addition reaction.

**Reduction of an aldehyde using  $\text{LiAlH}_4$  or  $\text{NaBH}_4$ :**

Reduction of an aldehyde using lithium aluminium hydride ( $\text{LiAlH}_4$ ) or sodium borohydride ( $\text{NaBH}_4$ ) gives the same organic compound like alcohols.

**Example:** acetaldehyde to ethanol. Reduction of an aldehyde leads to primary alcohol.



**Reduction of a ketone using  $\text{LiAlH}_4$  or  $\text{NaBH}_4$ :**

Reduction of a Ketone using lithium aluminium hydride ( $\text{LiAlH}_4$ ) or sodium borohydride ( $\text{NaBH}_4$ ) gives the same organic compound like alcohols.

**Example:** Acetone to iso-propyl alcohol. Reduction of a ketone leads to secondary alcohol.

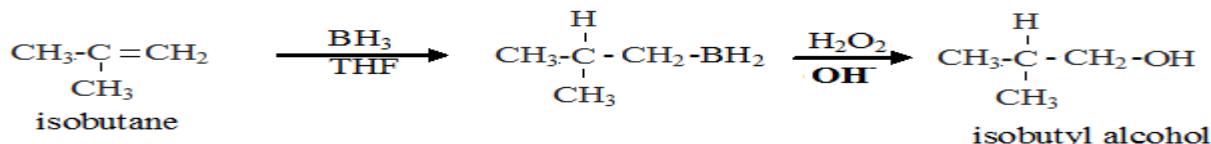
UNIT-IV



## HYDROBORATION OF OLEFINS

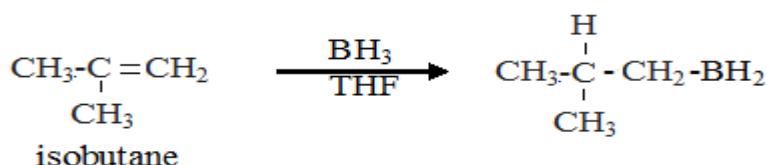
Hydroboration-Oxidation reaction is a two step organic reaction that converts an alkene into neutral alcohol by the net addition of water across the double bond. The hydrogen and hydroxyl group are added in a syn addition. Hydroboration-Oxidation reaction is an Anti Markovnikoff reaction with the hydroxyl group attaching to the less substituted carbon.

**Example:** Conversion of isobutane into isobutyl alcohol.

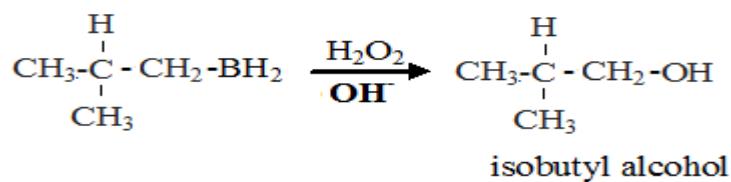


### **Mechanism of Hydroboration of olefins:**

**Step-1(Hydroboration):** In the step-1, borane ( $\text{BH}_3$ ) adds to the double bond transferring one of the hydrogen atoms to the carbon adjacent to the one that becomes bonded to the boron.



**Step-2 (Oxidation):** In the step-2, the nucleophilic hydroperoxide anion attacks the boron atom to give alcohol.



**SYNTHESIS OF ASPIRIN**

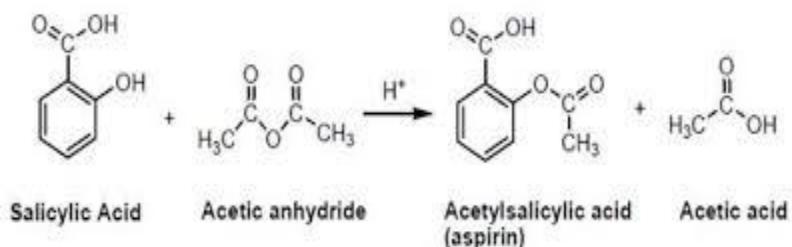
**Aim:** To prepare Aspirin from salicylic acid.

**Chemicals:** salicylic acid 2.5grams, acetic anhydride-5 ml and 3-4 drops Con.Sulphuric acid.

**Apparatus:** Conical flask, Measuring cylinder and filter paper.

**Principle:** Aspirin is prepared from salicylic acid by acetylating it with acetic anhydride in the presence of 3-4 drops of Con.Sulphuric acid as catalyst.

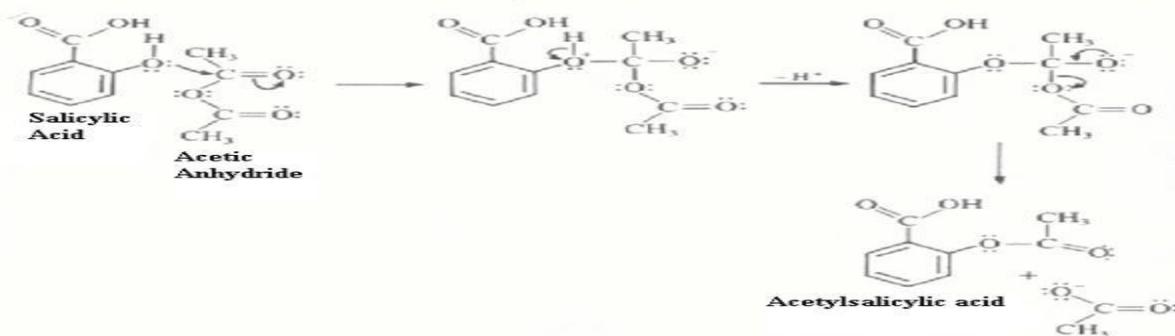
**Reaction:**



**Procedure:**

- Weigh 2.5 grams of salicylic acid and transfer to a 100ml cleaned and dried conical flask.
- Add 5ml of acetic anhydride and 3-4 drops Con.Sulphuric acid in to the flask.
- The contents of the flask should be thoroughly mixed.
- Warm the mixture on a water-bath maintaining 60 °C for about 20-25 min with constant stirring.
- Allow the contents of the flask to attain room temperature and pour it directly into a beaker having 100 ml cold water.
- Filter the crude product by using filter paper and dry it in hot air oven at 100 °C.
- Finally calculate yield of the Aspirin.

**Mechanism:**



## UNIT-IV

### Calculation:



Therefore, 2.5 grams of salicylic acid will form .....? (X) g Aspirin

$$X = (180 \times 2.5) / 138 = 3.26 \text{ g}$$

Theoretical yield = 3.26 g

$$\% \text{ Yield} = (\text{Practical Yield}) / (\text{Theoretical Yield}) \times 100$$

### Result:

1. Practical weight of the Aspirin \_\_\_\_\_ gm.

2. % yield of the Aspirin \_\_\_\_\_ %

## SYNTHESIS OF PARACETAMOL

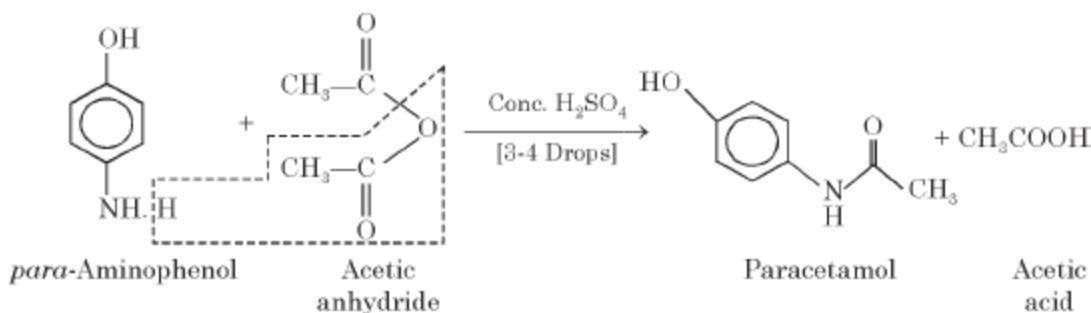
**Aim:** To prepare Paracetamol from p-aminophenol.

**Chemicals:** p-aminophenol-6grams, Acetic anhydride-6.5 ml and 3-4 drops Con.Sulphuric acid.

**Apparatus:** Conical flask, Measuring cylinder and filter paper.

**Principle:** Paracetamol is prepared from p-aminophenol by acetylating it with acetic anhydride in the presence of 3-4 drops of Con.Sulphuric acid as catalyst.

#### Reaction:

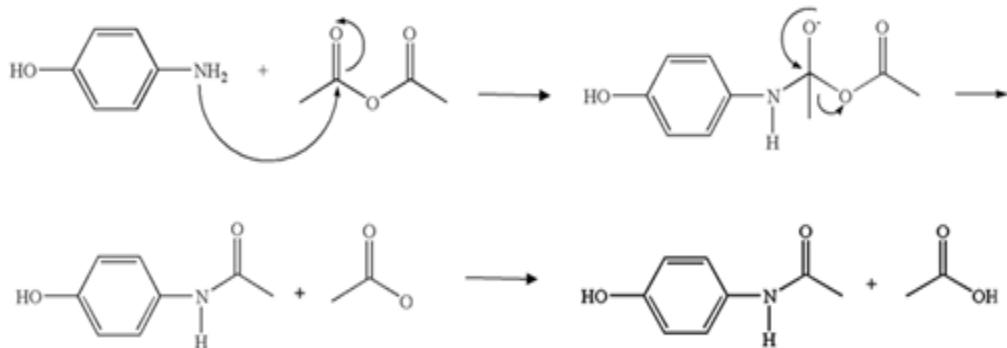


### Procedure:

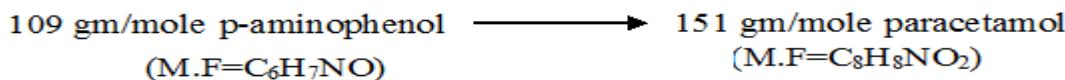
- Weigh 6 grams of p-aminophenol and transfer to a 100ml cleaned and dried conical flask.
- Add 6.5ml of acetic anhydride and 3-4 drops Con.Sulphuric acid in to the flask.
- The contents of the flask should be thoroughly mixed.

- Warm the mixture on a water-bath maintaining 60 °C for about 20-25 min with constant stirring.
- Allow the contents of the flask to attain room temperature and pour it directly into a beaker having 100 ml cold water.
- Filter the crude product by using filter paper and dry it in hot air oven at 100 °C.
- Finally calculate yield of the paracetamol.

**Mechanism:**



**Calculation:**



Therefore, 6 g p-aminophenol will form .....? (X) g paracetamol

$$X = (151 \times 6)/109 = 8.31 \text{ g}$$

Theoretical yield = 8.31 g

% Yield = (Practical Yield)/(Theoretical Yield) × 100

**Result:**

3. Practical weight of the Paracetamol \_\_\_\_\_ gm.

4. % yield of the Paracetamol \_\_\_\_\_ %

## *Learning objectives:*

**After completion of this unit the student should be able to:**

- Introduction to representation of 3-dimensional structures.
- Structural and stereoisomers.
- Configurations, symmetry and chirality.
- Enantiomers, diastereomers, optical activity.
- Absolute configuration. Conformation analysis of n- butane.

**Nucleophilic Substitution reactions:**

- Mechanism of S<sub>N</sub>1, S<sub>N</sub>2 reactions.
- Electrophilic and nucleophilic addition reactions:
- Addition of HBr to propene. Markownikoff and anti Markownikoff's additions.
- Grignard additions on carbonyl compounds.

**Elimination reactions:**

- Dehydro halogenation of alkylhalides. Saytzeff rule.

**Oxidation reactions:**

- Oxidation of alcohols using KMnO<sub>4</sub> and chromic acid.

**Reduction reactions:**

- Reduction of carbonyl compounds using LiAlH<sub>4</sub> & NaBH<sub>4</sub>.
- Hydroboration of olefins.

**Synthesis of drug molecules:**

- Structure, synthesis and pharmaceutical applications of Paracetamol.
- Structure, synthesis and pharmaceutical applications of Aspirin.

## *Short Answer Questions:*

**1.**Distinguish between Electrophilic addition reactions and nucleophilic addition reactions.

**2.**Explain Addition of HBr to propene by Markownikoff additions.

**3.**Write the Reduction of carbonyl compounds using NaBH<sub>4</sub>.

**4.**Explain Dehydro halogenation of alkylhalides with Saytzeff rule.

**5.**Give one example for Hydroboration of Olefins.

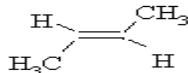
## UNIT-IV

6. Discuss the Oxidation of alcohols using chromic acid.
7. Explain Reduction of carbonyl compounds using  $\text{LiAlH}_4$ .
8. Explain Addition of HBr to propene by Markownikoff additions.
9. Write about optical activity with one example.
10. Define Diastereomers explain with one example.
11. Write about classification of isomers.
12. Define Enantiomers explain with one example.

### ***Descriptive Questions:***

1. Detail explanation of the Nucleophilic substitution reaction mechanism of  $\text{S}_{\text{N}}1$ ,  $\text{S}_{\text{N}}2$  reactions.
2. Describe the Oxidation of alcohols using  $\text{KMnO}_4$  and Chromic acid.
3. Explain Structure, synthesis and pharmaceutical applications of Aspirin.
4. Explain the following:
  - i. Electrophilic addition reaction (Addition of HBr to propene by Markownikoff-rule).
  - ii. Nucleophilic addition reaction (Grignard additions on carbonyl compound)
5. Explain Structure, synthesis and pharmaceutical applications of Paracetamol.
6. Explain Conformational analysis of n-butane.

### ***Objective Questions:***

1. Stereo chemistry explains the orientation of molecules in which of the following dimensional. [c]  
(a) 1D      (b) 2D      (c) 3D      (d) All
2. Write the name of this structure [b]  
  
(a) Cis-isomer      (b) Trans-isomer      (c) Enantiomer      (d) Diastereomer
3. Pair of molecules that are non-superimposable mirror images of each other is called [a]  
(a) Enantiomer      (b) Diastereomer      (c) Anomer      (d) Epimer
4. Which of the following compounds involved in nucleophilic addition reactions? [c]  
(a) Acetaldehyde      (b) Acetone      (c) Both      (d) Ethylene

## UNIT-IV

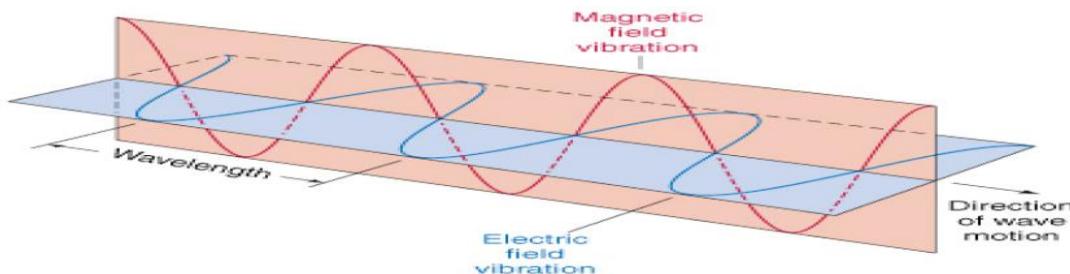
5. When Methyl Magnesium Bromide reacts with acetone which of the following alcohol will be formed. [c]  
(a)  $1^\circ$ -Alcohol (b)  $2^\circ$ -Alcohol (c)  $3^\circ$ -Alcohol (d)  $4^\circ$ -Alcohol
6. The number of steps involved in Bimolecular nucleophilic substitution reaction is... [a]  
(a) 1 (b) 2 (c) Both (d) 3
7. Which of the following product is obtained when acetaldehyde is undergone reduction with  $\text{LiAlH}_4$ . [d]  
(a) Formic acid (b) Acetic acid (c)  $\text{CO}_2$  (d) Ethanol
8. Which of the following chemicals are used for preparation of Aspirin. [c]  
(a) Salicylic acid (b) Acetic anhydride (c) Both (d) Acetic acid
9. According to the Anti-markownikoff rule, when 2-Butene is reacted with KBr which of the following is the major product. [a]  
(a) 1-bromo butane (b) 2-bromo butane (c) Both (d) 2-bromo butane
10. According to the Saytzeff's rule, which of the following is the major product is formed, when 2-chloro butane is reacted with alcoholic KOH is.. [b]  
(a) 1- butene (b) 2- butene (c) Both (d) 2- butanol

***Fill in the blanks:***

1. 2-chloropropane and 1-chloropropane are position isomers.
2. Plane Polarized Light is the full form of PPL in optical isomerism.
3. Unsaturated Hydrocarbon involved in electrophilic addition reactions.
4. Tertiary (  $3^\circ$  ) alkyl halide involved in uni molecular nucleophilic substitution reaction.
5. Hydrogen and Halide are eliminated in dehydrohalogenation reaction.
6. Acetic Acid obtained when acetaldehyde is undergone oxidation with  $\text{KMnO}_4$ .
7. Alcohols obtained by hydroboration of olefins.
8. P-Amino Phenol and Acetic anhydride chemicals are used in preparation of Paracetamol.
9. According to the Markownikoff rule, when 2-Butene is reacted with KBr 2-Bromo butane is the major product.
10. Alkyl magnesium halide is called Grignard reagent.

## INTRODUCTION TO SPECTROSCOPY

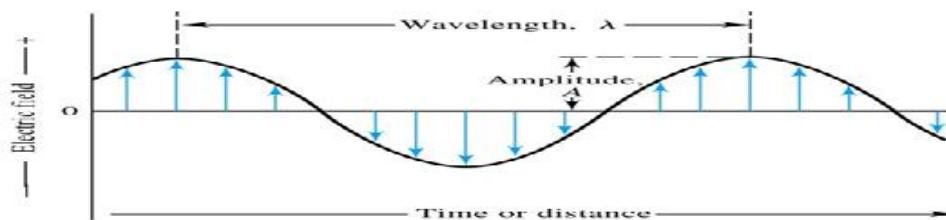
Spectroscopy is a method of analysis based on the interaction, absorption (or) production of light by matter. (Also may include the interaction of electrons, ions or acoustics with matter)



## TERMS IN ELECTRO MAGNETIC RADIATION

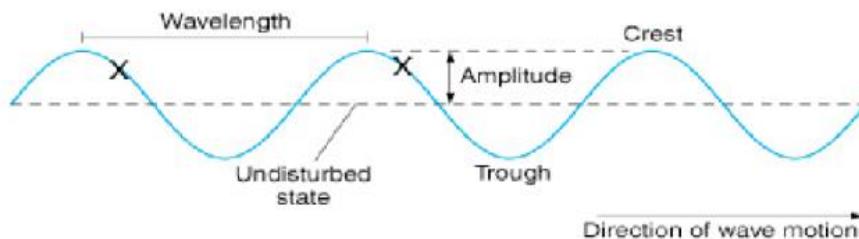
### 1) Amplitude (A):

- Amplitude is the distance from the maximum vertical displacement of the wave to the middle of the wave.
- This measures the magnitude of oscillation of a particular wave. In short, the amplitude is basically the height of the wave.



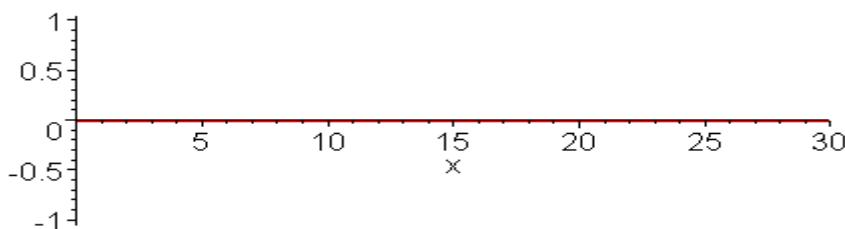
### 2) Wavelength ( $\lambda$ ):

- Wavelength is the distance of one full cycle of the oscillation.
- Longer wavelength waves such as radio waves carry low energy; this is why we can listen to the radio without any harmful consequences.
- Shorter wavelength waves such as x-rays carry higher energy that can be hazardous to our health. Consequently lead aprons are worn to protect our bodies from harmful radiation when we undergo x-rays.
- Units: Distance (nm, cm and m) from peak to peak.



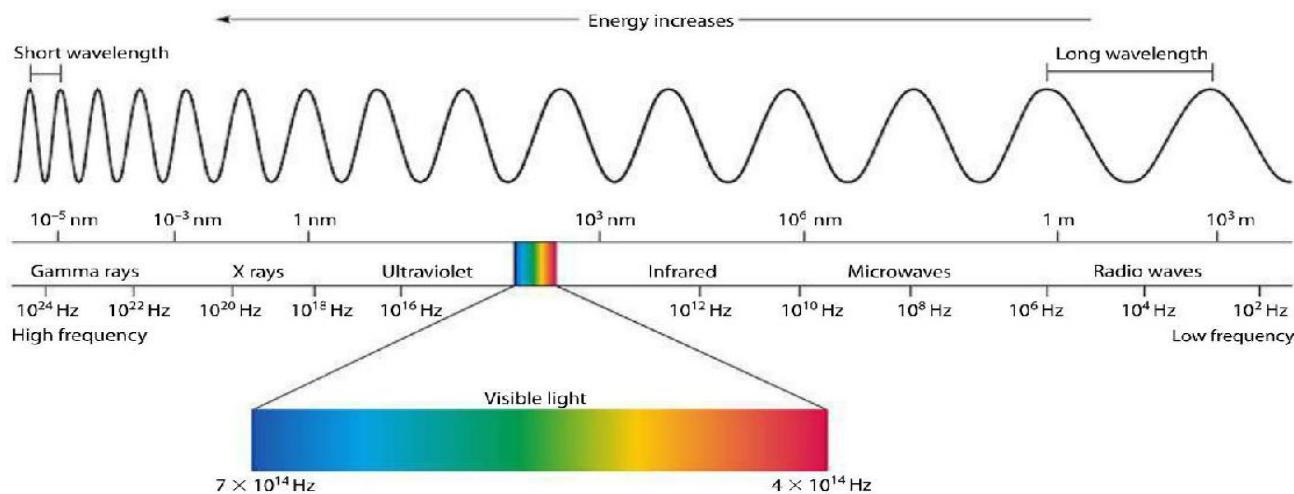
### 3) Frequency (n):

- Frequency is defined as the number of cycles per second,
- Frequency is directly proportional to energy and can be express as:
- Units:  $\text{sec}^{-1}$  or Hertz (Hz).



### WIDE RANGE OF TYPES OF ELECTROMAGNETIC RADIATION

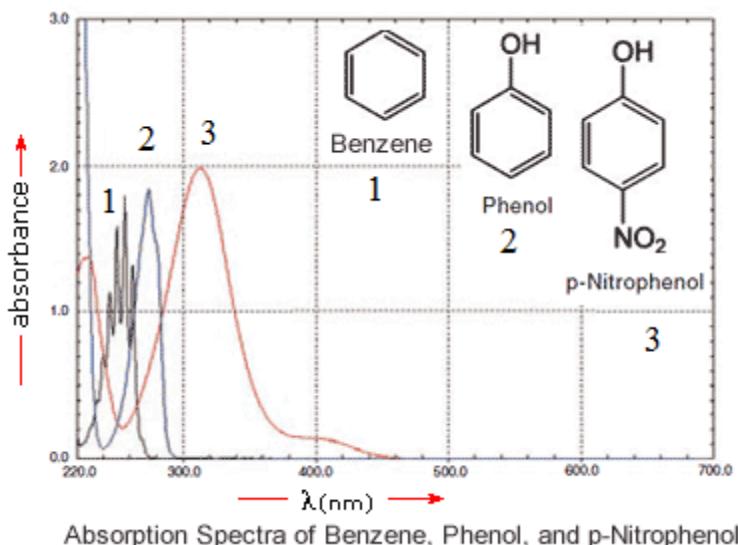
- As a wave's wavelength increases, the frequency decreases, and as wave's wavelength decreases, the frequency increases.
- When electromagnetic energy is released as the energy level increases, the wavelength decreases and frequency increases.
- Thus, electromagnetic radiation is then grouped into categories based on its wavelength or frequency into the electromagnetic spectrum.
- The different types of electromagnetic radiation shown in the electromagnetic spectrum consists of radio waves, microwaves, infrared waves, visible light, ultraviolet radiation, X-rays, and gamma rays.
- The part of the electromagnetic spectrum that we are able to see is the visible light spectrum.



## INTRODUCTION TO UV SPECTROSCOPY

UV spectroscopy is an important tool in analytical chemistry. The other name of UV (Ultra-Violet) spectroscopy is Electronic spectroscopy, as it involves the promotion of the electrons from the ground state to the higher energy or excited state.

UV spectroscopy is type of absorption spectroscopy in which light of ultra-violet region (200-400 nm.) is absorbed by the molecule. Absorption of the ultra-violet radiations results in the excitation of the electrons from the ground state to higher energy state.



Absorption Spectra of Benzene, Phenol, and p-Nitrophenol

Class	transition	Wavelength (nm) max
R-OH	$n \rightarrow \sigma^*$	180
R-O-R	$n \rightarrow \sigma^*$	180
R-NH <sub>2</sub>	$n \rightarrow \sigma^*$	190
R-SH	$n \rightarrow \sigma^*$	210
R <sub>2</sub> C=CR <sub>2</sub>	$\pi \rightarrow \pi^*$	175
R-C≡C-R	$\pi \rightarrow \pi^*$	170

## PRINCIPLE OF UV SPECTROSCOPY

UV spectroscopy obeys the Beer-Lambert law, which states that:

When a beam of monochromatic light is passed through a solution of an absorbing substance, the rate of decrease of intensity of radiation with thickness of the absorbing solution is proportional to the incident radiation as well as the concentration of the solution.

The expression of Beer-Lambert law is:  $A = \log(I_0/I) = Ecl$

**A** = absorbance

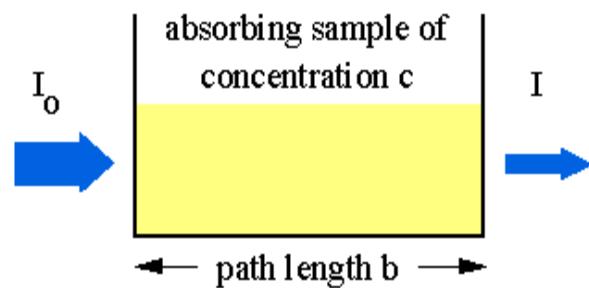
**I<sub>0</sub>** = intensity of light incident upon sample cell

**I** = intensity of light leaving sample cell

**C** = molar concentration of solute

**L** = length of sample cell (cm)

**E** = molar absorptivity.



From the Beer-Lambert law it is clear that greater the number of molecules capable of absorbing light of a given wavelength, the greater the extent of light absorption. This is the basic principle of UV spectroscopy.

### **INSTRUMENTATION AND WORKING OF UV SPECTROSCOPY**

Instrumentation and working of the UV spectrometers can be studied simultaneously. Most of the modern UVspectrometers consist of the following parts:

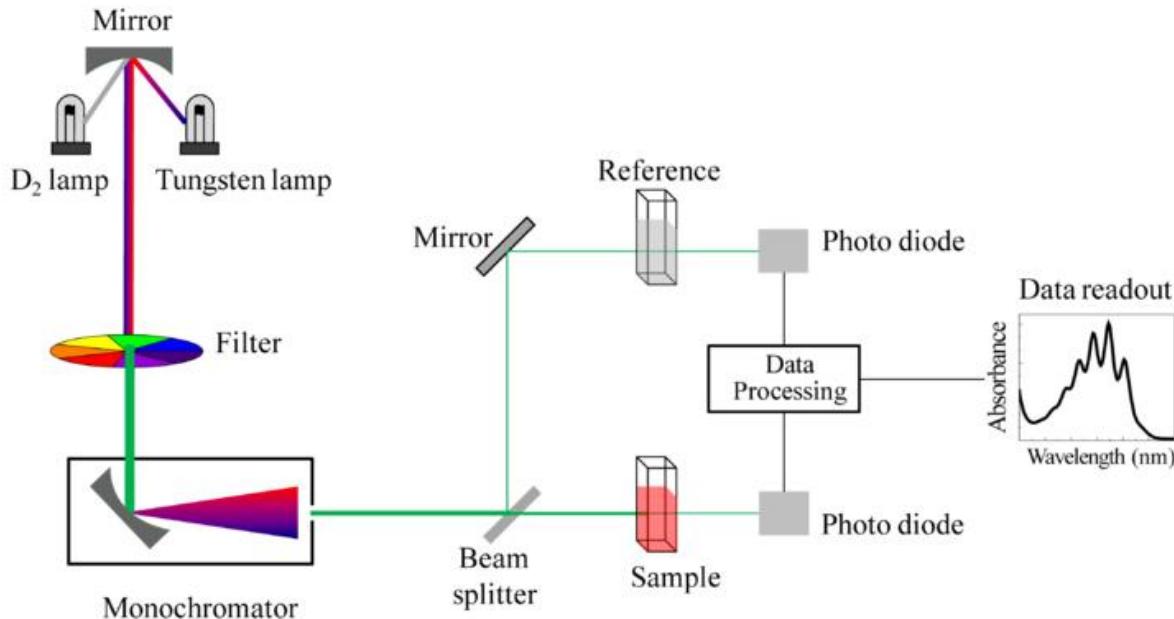
**1. Light Source:** Tungsten filament lamps and Hydrogen-Deuterium lamps are most widely used and suitable light source as they cover the whole UV region. Tungsten filament lamps are rich in red radiations. More specifically they emit the radiations of 375 nm, while the intensity of Hydrogen-Deuterium lamps falls below 375 nm.

**2. Monochromator:** Monochromators generally composed of prisms and slits. The most of the spectrophotometers are **double beam spectrophotometers**. The radiation emitted from the primary source is dispersed with the help of rotating prisms. The various wavelengths of the light source which are separated by the prism are then selected by the slits such the rotation of the prism results in a series of continuously increasing wavelength to pass through the slits for recording purpose. The beam selected by the slit is monochromatic and further divided into two beams with the help of another prism.

**3. Sample and reference cells:** One of the two divided beams is passed through the sample solution and second beam is passé through the reference solution. Both sample and reference solution are contained in the cells.

These cells are made of either silica or quartz. Glass can't be used for the cells as it also absorbs light in the UV region.

**4. Detector:** Generally two photocells serve the purpose of detector in UV spectroscopy. One of the photocell receives the beam from sample cell and second detector receives the beam from the



reference. The intensity of the radiation from the reference cell is stronger than the beam of sample cell. This results in the generation of pulsating or alternating currents in the photocells.

**5. Recording devices:** Most of the time amplifier is coupled to a pen recorder which is connected to the computer. Computer stores all the data generated and produces the spectrum of the desired compound.

### **SELECTION RULES OF UV SPECTROSCOPY**

**1. Laporte selection rule:** There must be a change in the symmetry of the complex Electric dipole transition can occur only between states of opposite symmetry.

Laporte-allowed transitions:       $g \rightarrow u$  (or)  $u \rightarrow g$

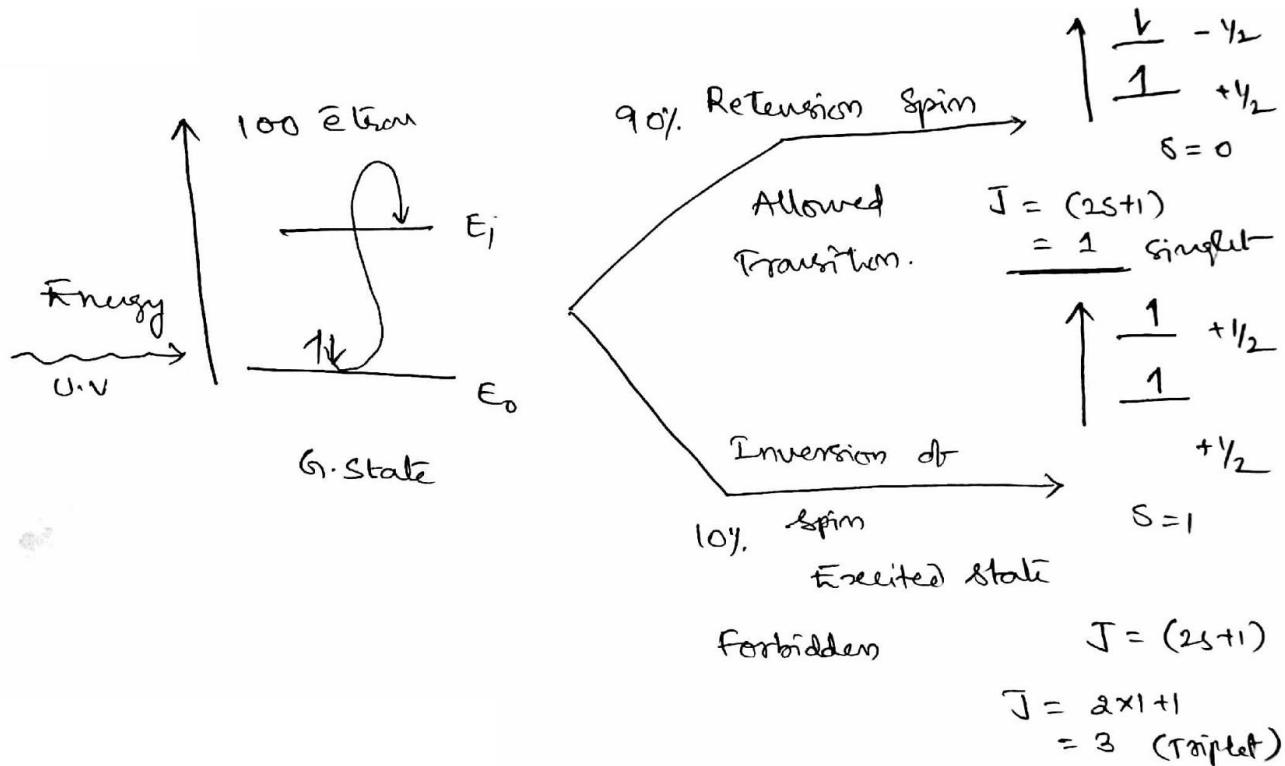
Laporte-forbidden transitions:       $g \rightarrow g$  (or)  $u \rightarrow u$

'g' stands for gerade – compound with a center of symmetry, 'u' stands for ungerade – compound without a center of symmetry.

**2. Spin Selection Rule:** The overall spin 'S' of a complex must not change during an electronic transition, hence,  $\Delta S = 0$ .

$$J = [2S+1] \quad \text{where, } J = \text{spin multiplicity, } S = \text{electron spin}$$

Electron transitions with retention of spin orientation is allowed, with inversion of spin orientation is Forbidden transition this is known as spin exclusion principle.

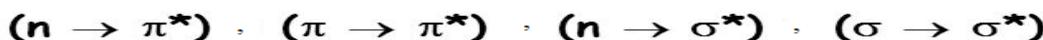


Electron transitions with retention of spin multiplicity are allowed transition. Electron transitions with inversion of spin multiplicity are forbidden transition.

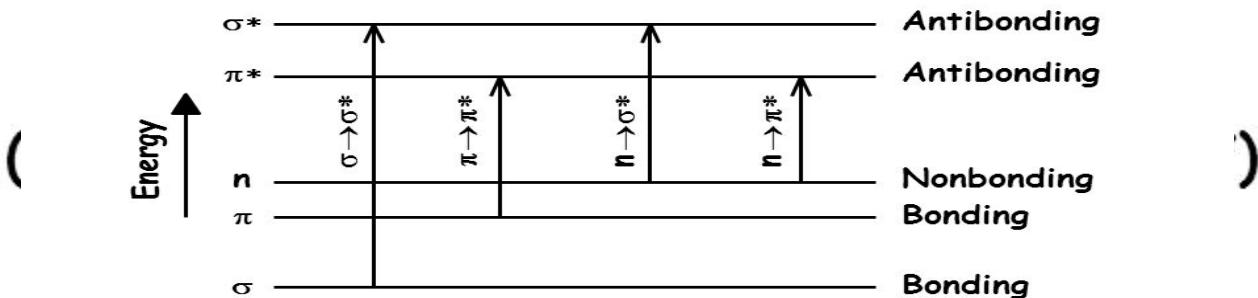
### 3. Selection rule based on transition from HOMO to LUMO:

- Generally, the most favoured transition is from the highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO).
- For most of the molecules, the lowest energy occupied molecular orbitals are **s orbital**, which correspond to **sigma bonds**. The **p orbitals** are at somewhat higher energy levels, the orbitals (nonbonding orbitals) with unshared paired of electrons lie at higher energy levels.
- The unoccupied or antibonding orbitals ( $\pi^*$  and  $\sigma^*$ ) are the highest energy occupied orbitals. In all the compounds (other than alkanes), the electrons undergo various transitions.

- Some of the important transitions with increasing energies are:



**Bonding electrons appear in  $\sigma$  and  $\pi$  molecular orbitals  
nonbonding in  $n$**



**Electronic transitions can occur between various states.  
The energy of the transitions increases in the following order:**



## CONCEPT OF CHROMOPHORE AND AUXOCHROME IN THE UV SPECTROSCOPY

**1. Chromophore** is defined as any isolated covalently bonded group that shows a characteristic absorption in the **ultraviolet or visible region (200-800 nm)**. Chromophores can be divided into two groups:

a. Chromophores which contain  $\pi$  electrons and which undergo  $\pi-\pi^*$  transitions.

Ex: Ethylenes and acetylenes

b. Chromophores which contain both  $\pi$ - electrons and  $n$  (non-bonding) electrons undergo two types of transitions:  $\pi-\pi^*$  and  $n-\pi^*$ .

Ex: Carbonyl, nitriles, azo compounds, nitro compounds etc.

**2. Auxochromes:** An auxochrome can be defined as any group which does not itself act as a chromophore but whose presence brings about a shift of the absorption band towards the longer wavelength of the spectrum.

Ex:  $-\text{OH}$ ,  $-\text{OR}$ ,  $-\text{NH}_2$ ,  $-\text{NHR}$ ,  $-\text{SH}$  etc.

All auxochromes have one or more non-bonding pairs of electrons. If an auxochrome is attached to a chromophore, it helps in extending the conjugation by sharing of non-bonding pair of electrons

Ex: When the auxochrome  $-\text{NH}_2$  group is attached to benzene ring. Its absorption change from  $\lambda_{\text{max}} 225$  to  $\lambda_{\text{max}} 280$ .

**ABSORPTION AND INTENSITY SHIFTS IN THE UV SPECTROSCOPY**

Absorption and intensity shifts are four types:

**a) Bathochromic effect (Red shift):**

Bathochromic shift is an effect by virtue of which the **absorption maximum is shifted towards the longer wavelength** due to the presence of an auxochrome (or) change in solvents. The  $n-\pi^*$  transition of carbonyl compounds observes bathochromic (or) red shift.

**Ex:** The  $n \rightarrow \pi^*$  transition for carbonyl compound gives bathochromic shift (increasing of wavelength) when the polarity of solvent is decrease, the negatively charge present on oxygen atom delocalized more due to red shift.

**b) Hypsochromic shift (Blue shift):**

This type of shift is an effect by virtue of which **absorption maximum is shifted towards the shorter wavelength**.

Generally it is caused due to the removal of conjugation (or) by changing the polarity of the solvents.

**Ex:** Aniline shows blue shift (decreasing of wavelength) in acidic medium and an unshared pair on nitrogen of aniline is not available for delocalization in cation, so that wavelength will be decrease.

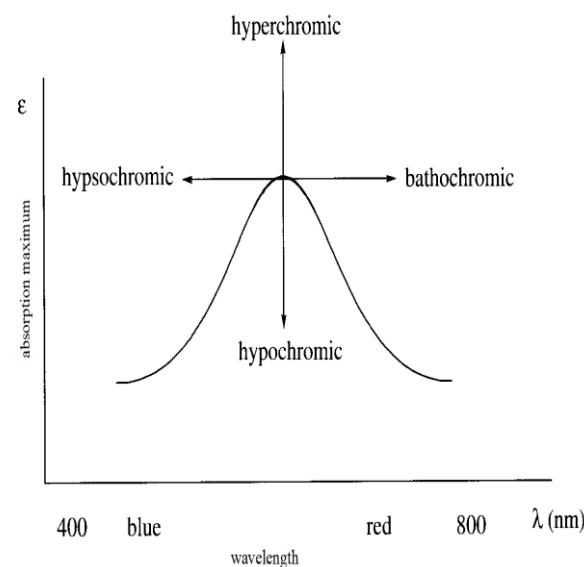
**c) Hyperchromic effect:** Hyperchromic shift is an effect by virtue of which **absorption maximum increases**.

The introduction of an auxochrome in the compound generally results in the hyperchromic effect.

**d) Hypochromic effect:**

Hypochromic effect is defined as the effect by virtue of **absorption maximum decreases**.

Hypochromic effect occurs due to the distortion of the geometry of the molecule with an introduction of new group.



## APPLICATIONS OF UV SPECTROSCOPY

### 1. Detection of functional groups:

UV spectroscopy is used to detect the presence or absence of chromophore in the compound. This technique is not useful for the detection of chromophore in complex compounds. The absence of a band at a particular band can be seen as an evidence for the absence of a particular group.

**Ex:** If the spectrum of a compound comes out to be transparent above 200 nm than it confirms the absence of \_\_\_\_\_.

- a) Conjugation b) A carbonyl group c) Benzene or aromatic compound **d) Bromo or iodo atoms.**

### 2. Detection of extent of conjugation:

The extent of conjugation in the polyenes can be detected with the help of UV spectroscopy. With the increase in double bonds the absorption shifts towards the longer wavelength. If the double bond is increased by 8 in the polyenes then that polyene appears visible to the human eye as the absorption comes in the visible region.

### 3. Identification of an unknown compound:

An unknown compound can be identified with the help of UV spectroscopy. The spectrum of unknown compound is compared with the spectrum of a reference compound and if both the spectrums coincide then it confirms the identification of the unknown substance.

### 4. Determination of configurations of geometrical isomers:

It is observed that **cis-alkenes** absorb at different wavelength than the **trans-alkenes**.

- The two isomers can be distinguished with each other when one of the isomers has non-coplanar structure due to steric hindrances.
- The cis-isomer suffers distortion and absorbs at lower wavelength as compared to trans-isomer.

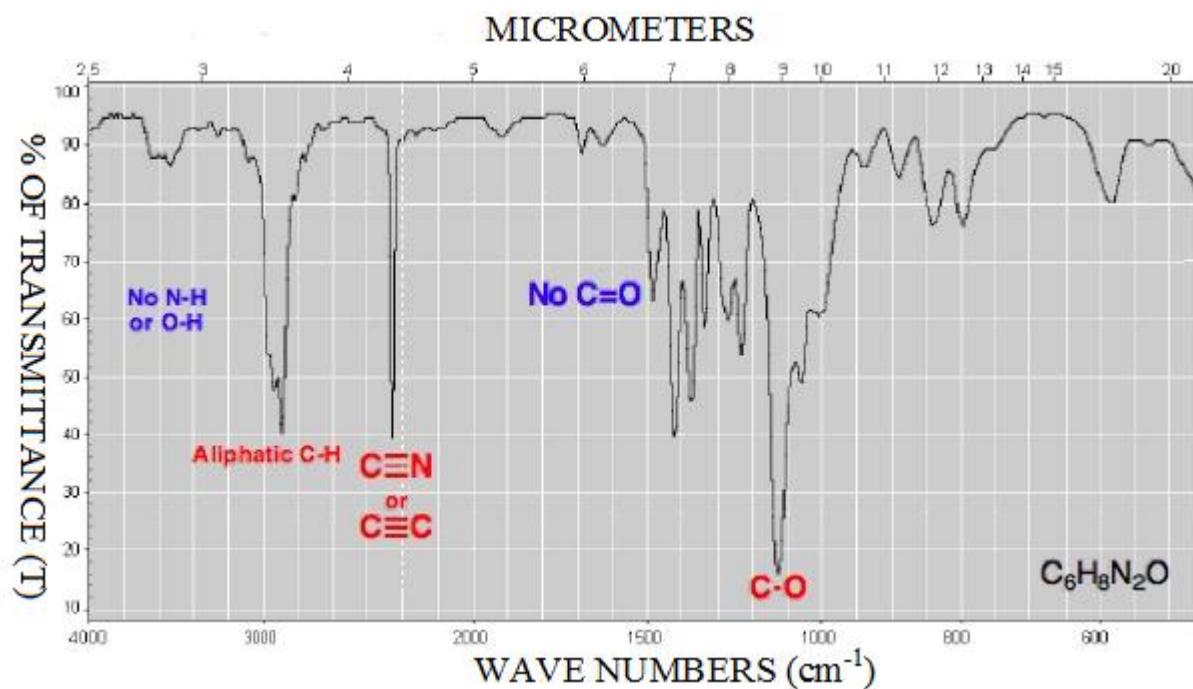
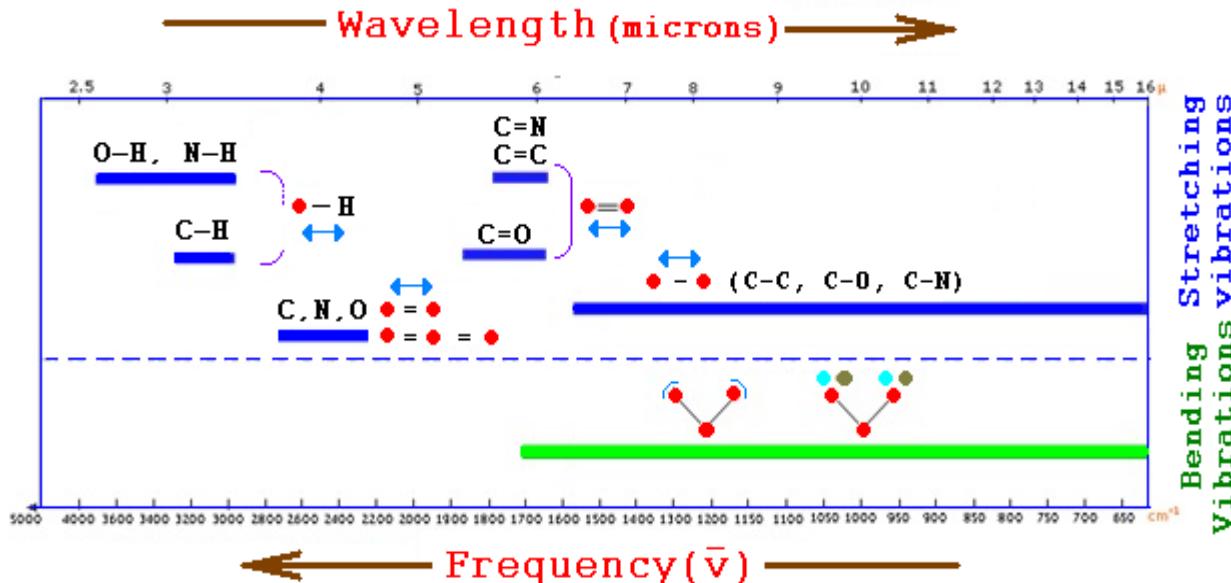
### 5. Determination of the purity of a substance:

Purity of a substance can also be determined with the help of UV spectroscopy. The absorption of the sample solution is compared with the absorption of the reference solution. The intensity of the absorption can be used for the relative calculation of the purity of the sample substance.

## INTRODUCTION TO IR SPECTROSCOPY

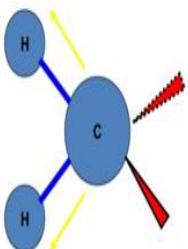
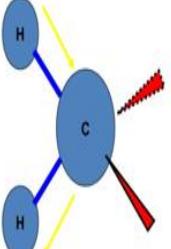
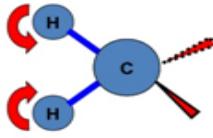
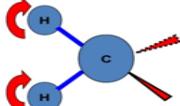
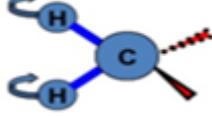
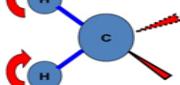
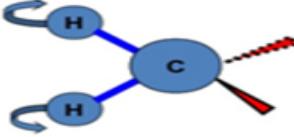
IR spectroscopy chart consist different regions of various kinds of vibrational bands. Absorption bands in the region are usually because of stretching vibrations of diatomic units.

1. Group frequency region is the region from 4000 to 1450  $\text{cm}^{-1}$ .
2. Fingerprint region is the region from 1450 to 600  $\text{cm}^{-1}$ .



## STRETCHING AND BENDING VIBRATIONS

IR radiation does not have enough energy to induce electronic transitions as seen with UV. Absorption of IR is restricted to compounds with small energy differences in the possible **vibration and rotational states**. Vibrations are two types as follows:

Stretching-Vibrations	Bending Vibrations.
<ul style="list-style-type: none"> <li>Stretching Vibrations are formed due to the vibration along the line of bond.</li> <li>Bond length will be change due to stretching vibrations.</li> <li>It occurs at higher energy (<math>4000\text{-}1250\text{cm}^{-1}</math>).</li> <li>These are two types:           <ul style="list-style-type: none"> <li>a. Symmetrical stretching.</li> <li>b. Asymmetrical stretching.</li> </ul> </li> <li>In <b>symmetrical stretching</b> two bonds length increase (or) decrease in simultaneously.</li> </ul> <div style="display: flex; justify-content: space-around; align-items: center;">   </div> <ul style="list-style-type: none"> <li>In <b>asymmetrical stretching</b>, one bond length increases and other bond length decreases.</li> </ul> <div style="display: flex; justify-content: space-around; align-items: center;">   </div>	<ul style="list-style-type: none"> <li>Bending Vibrations are formed due to the vibration not along the line of bond.</li> <li>Bond length will not be change due to bending vibrations.</li> <li>It occurs at lower energy (<math>1400\text{-}666\text{cm}^{-1}</math>).</li> <li>These are two types:           <ul style="list-style-type: none"> <li>a. In plane bending (scissoring and rocking)</li> <li>b. out plane bending (wagging and twisting).</li> </ul> </li> <li>In <b>scissoring</b> the bond angles are decreases.</li> <div style="display: flex; justify-content: space-around; align-items: center;">   </div> <li>In <b>rocking</b> the movement of atoms takes place in the same direction.</li> <div style="display: flex; justify-content: space-around; align-items: center;">   </div> <li>In <b>wagging</b> two atoms move to one side of the plane and they move up and down the plane.</li> <div style="display: flex; justify-content: space-around; align-items: center;">   </div> <li>In <b>twisting</b> one atom moves above the plane and another atom moves below.</li> <div style="display: flex; justify-content: space-around; align-items: center;">   </div> </ul>

## PRINCIPLE OF IR SPECTROSCOPY

Infra-red spectroscopy is an important spectroscopy which gives almost complete information about the **structure of a compound**. The infra-red spectrum is containing a large number of absorption bands which provides much information about the molecule's structure.

The absorption of infrared radiations can be expressed either in terms of **wavelength** or **wave number**.

$$\text{Wave length (cm)} = 1/\text{wave number (cm}^{-1}\text{)}$$

The intensity of bands observed in IR spectrum is expressed in terms of **transmittance (T)** or **absorbance (A)**.

$$A = \log_{10} (1/T)$$

Because of absorption of infra-red radiation, molecules become excited and move to lower to higher vibrational level. Each vibrational level is associated with a number of spaced rotational levels. Hence the absorption of infra-red caused to effect vibrational as well as rotational level and also called as vibrational- rotational spectra.

Region	Wavelength range (nm)	Wave number range (cm <sup>-1</sup> )
Near	0.78 - 2.5	12800 – 4000
Middle	2.5 – 50	4000 – 200
Far	50 - 1000	200 - 10

## INSTRUMENTATION AND WORKING OF IR SPECTROSCOPY

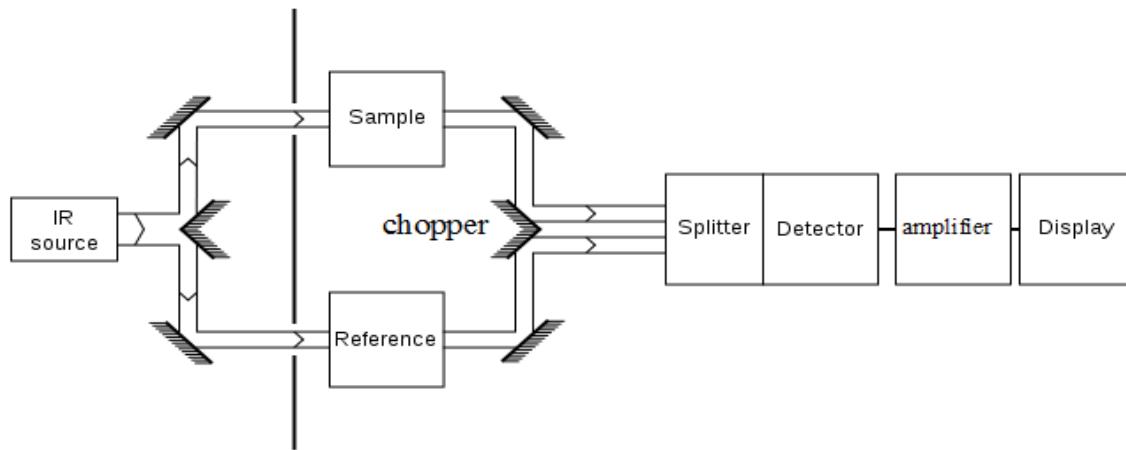
There are mainly two components in IR spectroscopy instrument, Source and detectors.

**Source** of IR spectrometer is **Nernst glower** (mixture of the oxides of Zr, Y and Er) and another source is **Globar(SiC)**

- The rod is electrically heated upto **1773° K** temperature to produce Infrared radiations; to change these IR radiations to monochromatic light, optical prism (or) grating can be used.
- Sodium chloride (or) other alkali metal halides is the best material to form prism.
- Cell container as they are transparent in Infra-red region. Light beam is split into two beams; one is **sample beam** and another beam is the **reference beam**. Due to absorption of radiation

by sample compound, the intensity of sample beam decreases. Hence there will be some difference in intensity of reference beam and sample beam.

- These two beams allow to fall on the **segmented mirror (chopper)** with the help of two supporting mirror. The segmented mirror also known as **chopper** rotates at a definite speed reflects the sample and reference beams to a monochromatic grating.
- As the grating rotates, it sends individual frequencies to the detector **thermopile** which convert IR energy to electrical energy.
- This is then amplified by using **amplifier**. Because of the difference in intensity of both beams, alternating current starts flowing from the detector to amplifier.



- The amplifier is coupled with a small motor which drive an optical wedge and further coupled with a pen recorder used to draw absorption bands on the calibration chart.

### SELECTION RULES OF IR SPECTROSCOPY

The absorption of infrared radiations is possible by only those bonds of molecule which can show a change in **dipole moment** by the absorption of radiations. Such types of vibrational transitions which involve the change in dipole moment are known as **infra-red transitions**. However those vibrational transitions which are not accompanied by the change in dipole moment are not directly observed and called as infra-red inactive transition.

**Ex:** the vibrational transitions of C=O , O-H , N-H etc. bands are accompanied by the change in dipole moment, hence absorbed strongly in IR region.

While some other transitions like C-C bond in symmetrical alkene and alkyne are IR inactive transitions. Hence some of the fundamental vibrations are infra-red active and some are not. It is governed by the selection rule.

1. If a molecule has a center of symmetry, then the vibrations are Centro symmetric and are inactive in the infra-red region but active in Raman, known as active vibrations.
2. The vibrations which are not Centro symmetric are active in infra-red region but inactive in Raman, called as forbidden vibrations.
3. Since the absorption of infra-red region is quantized, a molecule of the organic compound will show a number of peaks in the infrared region.

**There are two important selection principles:**

1. Only those transitions are permitted in which the vibrational quantum number ( $v$ ) changes by  $+/-1$ . The transitions corresponding to this change are known as fundamental vibration tones. However vibrations of  $+/-2$ ,  $+/-3$ , etc. equivalent to harmonic tones are known as forbidden transitions, which are not permitted.
2. The absorption of radiation can be possible only when the dipole moment of the whole molecule changes due to certain molecular vibrations.

### **IR SPECTROSCOPY CHART**

IR spectroscopy chart consists of different regions of various kinds of vibrational bands. The region from 1450 to 600  $\text{cm}^{-1}$  is called as fingerprint region and the absorption bands in the 4000 to 1450  $\text{cm}^{-1}$  region are usually because of stretching vibrations of diatomic units, and known as the group frequency region.

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#### **IR Absorptions of Common Functional Groups**

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<b>Functional Group</b>	<b>Absorption Location (<math>\text{cm}^{-1}</math>)</b>
Alkane (C—H)	2,850–2,975
Alcohol (O—H)	3,400–3,700
Alkene (C=C) (C=C—H)	1,640–1,680 3,020–3,100
Alkyne (C≡C) (C≡C—H)	2,100–2,250 3,300
Nitrile (C≡N)	2,200–2,250
Aromatics	1,650–2,000
Amines (N—H)	3,300–3,350

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**APPLICATIONS OF IR SPECTROSCOPY**

This technique is quite useful to predict the presence of certain functional groups which absorb at definite frequencies. It is widely used in different industries like organic synthesis, agriculture soil analysis and biochemical industries for the analysis of complex biological molecules like proteins, nucleic acid and lipids.

The main benefit of this technique is that some of the applications of IR spectroscopy are as follows.

**1. Identification of functional group and structure elucidation:**

- The identity of an organic compound is confirmed if its finger print region ( $1400\text{-}1900\text{ cm}^{-1}$ ) exactly matches with the known spectrum of that compound.
- As compounds contain same functional group may have similar absorptions above  $1500\text{ cm}^{-1}$  but they differ considerably in finger print region.

**2. Identification of structure of substances:**

- Infra red spectroscopy is used to establish the structure of an unknown compound.
- All functional groups present in molecule absorbed at their characteristic wave number and the shift due to environment effect can be easily observed in spectrum.
- From the data available, the whole structure of molecule can be predicated.
- IR spectrum cannot identify the presence of Enantiomers as they show similar IR spectrum.

**3. Study of the progress of a chemical reaction:**

- Infra red spectroscopy is quite useful for studying the rate and progress of a chemical reaction.
- For example the reduction of ketone to secondary alcohol can be detected easily. As the absorption band of ketone is observed at about  $1710\text{ cm}^{-1}$ .
- With the progress of reaction the band of  $>\text{C=O}$  group diminished and band of  $\text{-OH}$  group at  $3300\text{ cm}^{-1}$  appears.

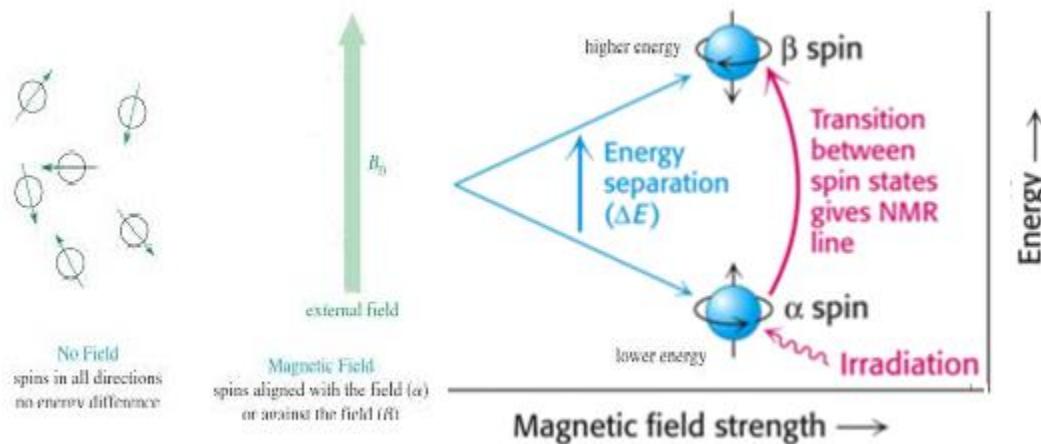
**4. Detection of impurities Infra-red:**

- Infra red spectroscopy is also useful in the detection of the impurity in a compound by comparing its spectrum with the spectrum of the authentic sample of the compound. A pure sample always consists of sharp peaks and bands while the impure sample will have poor bands with some additional bands.

**5. Quantitative analysis:** The quantitative analysis of an organic mixture can be done by measuring the intensities of the absorption bands of each component.

**PRINCIPLE OF NMR SPECTROSCOPY**

- The principle behind NMR is that many **nuclei have spin** and **all nuclei are electrically charged**.
- If an external magnetic field is applied, an energy transfer is possible between the base energy to a higher energy level (generally a single energy gap).
- The energy transfer takes place at a wavelength that corresponds to radio frequencies and when the spin returns to its base level, energy is emitted at the same frequency.
- The signal that matches this transfer is measured in many ways and processed in order to yield an NMR spectrum for the nucleus concerned.
- The principle of nuclear magnetic resonance is based on the **spins of atomic nuclei**.
- The magnetic measurements depend upon the spin of unpaired electron whereas nuclear magnetic resonance measures magnetic effect caused by the spin of protons and neutrons.
- Both these nucleons have intrinsic angular momenta (or) spins and hence act as elementary magnet.



- The existence of nuclear magnetism was revealed in the hyper fine structure of spectral lines.
- If the nucleus with a certain magnetic moment is placed in the magnetic field, we can observe the phenomenon of space quantization and for each allowed direction there will be a slightly different energy level.
- NMR active:  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{15}\text{N}$ ,  $^{19}\text{F}$ ,  $^{31}\text{P}$  etc.

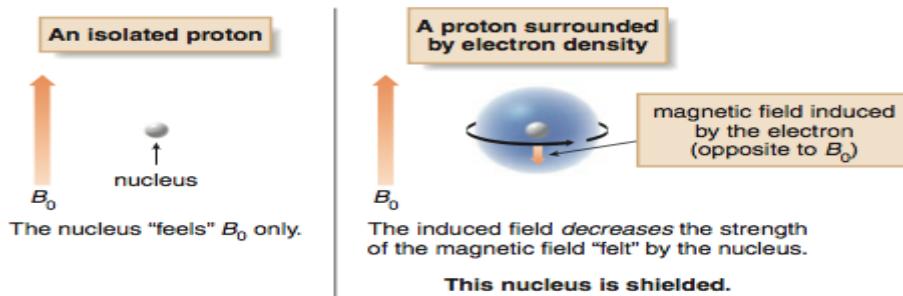
**SHIELDING AND DESHIELDING OF NMR SPECTROSCOPY**

The basic principle of NMR is to apply an **external magnetic field** called  $B_0$  and measure the frequency at which the nucleus achieves **resonance**.

Electrons orbiting around the nucleus generate a **small magnetic field that opposes  $B_0$** . In this case we say that **electrons are shielding the nucleus from  $B_0$** .

**Shielding:**

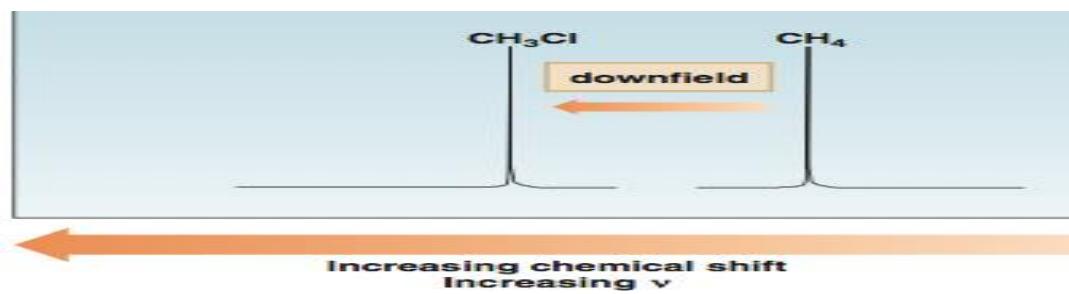
- The **higher the electron density around the nucleus**, the higher the opposing magnetic fields to  $B_0$  from the electrons, the **greater the shielding**.
- Because the **proton experiences lower external magnetic field**, it needs a **lower frequency to achieve resonance**, and therefore, the chemical shift shifts **upfield (lower ppms)**.

**Deshielding:**

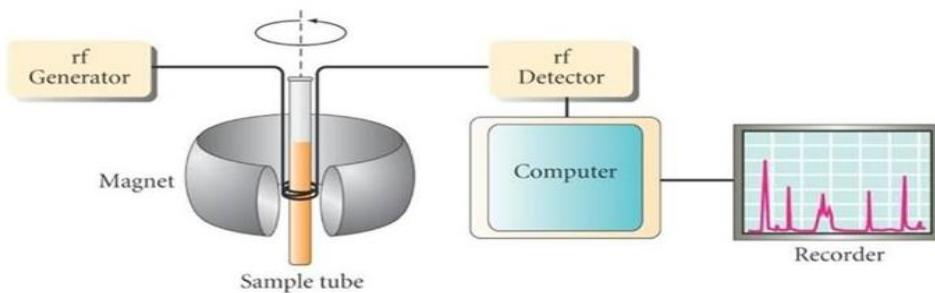
- If the **electron density around a nucleus decreases**, the opposing magnetic field becomes small and therefore, the nucleus feels more the external magnetic field  $B_0$ , and therefore it is said to be **deshielded**.
- Because the **proton experiences higher external magnetic field**, it needs a **higher frequency to achieve resonance**, and therefore, the chemical shift shifts **downfield (higher ppms)**.

**Example:** Let us compare the chemical shift of  $\text{CH}_4$  protons and  $\text{CH}_3\text{Cl}$  protons:

- Chlorine atom is an electronegative atom that will pull the electron density toward it (**electron withdrawing**), resulting in a **deshielding of the hydrogen nucleus**; an edit will fell higher external magnetic field  $B_0$  increasing the resonance frequency and therefore, shifting to higher ppms.
- Hydrogen nucleus is shielded in the case of  $\text{CH}_4$  and therefore, the peak appears on the lower ppm side.



## INSTRUMENTATION OF NMR SPECTROSCOPY



The most important parts of an FTNMR instrument are:

- Magnet
- RF generator
- Sample chamber or probe
- pulse generator
- RF receiver
- Computer for data processing

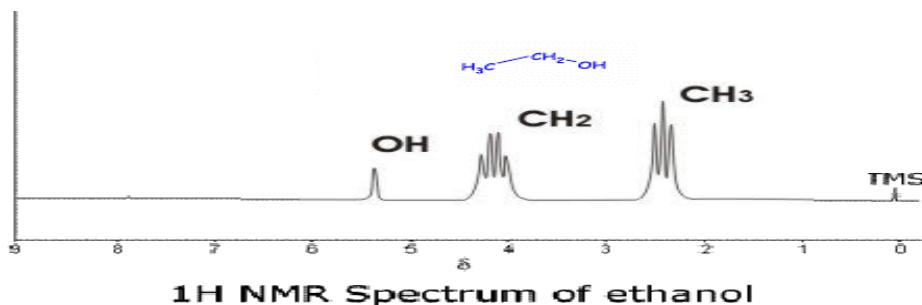
## SELECTION RULE OF NMR SPECTROSCOPY

In NMR splitting of the signal based on the  **$2nI+1$  rule**,

**Where:** I = spin of Hydrogen: H ( $\frac{1}{2}$ ), n = neighboring group.

$$2n \left(\frac{1}{2}\right) + 1 = n+1$$

**Ex: NMR signal of ethyl alcohol ( $\text{CH}_3\text{-CH}_2\text{-OH}$ ):**



$\text{CH}_3$  (**n+1rule where n=2hydrogens**):  $2+1=3$ (triplet)

$\text{CH}_2$  (**n+1rule where n=3hydrogens**):  $3+1=4$ (quartet)

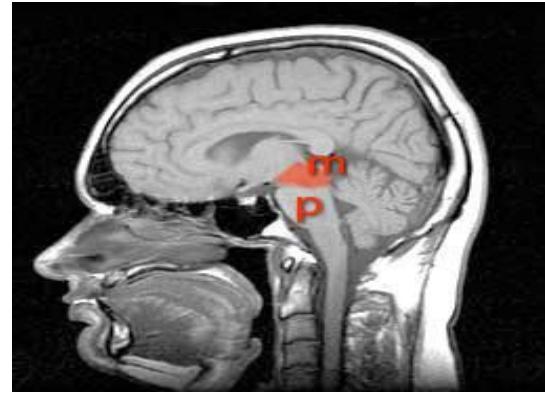
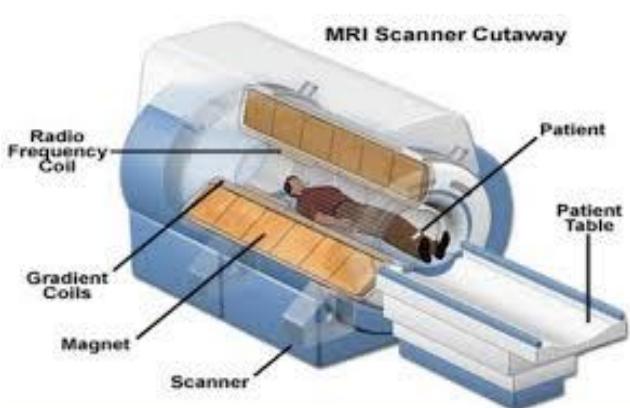
$\text{OH}$  (**n+1rule where n=0hydrogens**):  $0+1=1$ (singlet)

## **APPLICATIONS OF NMR SPECTROSCOPY**

- It is useful to detect total number of protons present in the molecule.
- It is useful to distinguish between Cis and Trans isomers.
- It is useful in detecting aromaticity of molecule.
- It is also used to detect Hydrogen bonding in the molecule.
- In NMR spectra, different peaks give information about different atoms in a molecule according specific chemical environments and bonding between atoms. The most common isotopes used to detect NMR signals are  $^1\text{H}$  and  $^{13}\text{C}$  but there are many others, such as  $^2\text{H}$ ,  $^3\text{He}$ ,  $^{15}\text{N}$ ,  $^{19}\text{F}$ , etc., that are also in use.
- NMR has also proven to be very useful in other area such as environmental testing, petroleum industry, process control, earth's field NMR and magnetometers.
- Non-destructive testing saves a lot of money for expensive biological samples and can be used again if more trials need to be run. The petroleum industry uses NMR equipment to measure porosity of different rocks and permeability of different underground fluids.
- Magnetometers are used to measure the various magnetic fields that are relevant to one's study.

## APPLICATIONS OF MAGNETIC RESONANCE IMAGING

The basic principle of MRI and NMR is the same. The mission of MRI makes use of the fact that the body tissue contains lot of water, the protons of which get aligned in a large magnetic field when a person is placed inside the powerful magnetic field of the machine; the protons align themselves with the direction magnetic field. This external magnetic field, applied on the nuclei, produce energy levels.



- Nuclear magnetic resonance imaging, better known as magnetic resonance imaging (MRI).
- It is an important medical diagnostic tool used to study the function and structure of the human body.
- It provides detailed images of any part of the body, especially soft tissue, in all possible planes and has been used in the areas of cardiovascular, neurological, musculoskeletal and iconological imaging.
- Unlike other alternatives, such as computed tomography (CT), it does not use ionized radiation and hence is very safe to administer.
- In many laboratories today, chemists use nuclear magnetic resonance to determine structures of important chemical and biological compounds.

**MRI is used to diagnose (or) monitor the treatment conditions like the following diseases:**

- Brain Tumors
- Trauma
- Infectious Diseases
- Pediatric Metabolic Disorders
- Alzheimer's disease

## ***Learning objectives:***

**After completion of this unit the student should be able to:**

- Principles of spectroscopy.
- Selection rules and applications of electronic spectroscopy.
- Selection rules and applications of vibrational spectroscopy.
- Selection rules and applications of rotational spectroscopy.
- Selection rules and applications NMR Spectroscopy.
- Nuclear magnetic resonance Spectroscopy - chemical shift.
- Introduction and Applications of Magnetic resonance imaging.

## ***Short Answer Questions:***

1. Define the term Auxochrome with example.
2. Explain the Selection rules of electronic spectroscopy.
3. Discuss the Selection rules of IR spectroscopy.
4. Write about Stretching and bending vibrations of molecules.
5. What are the applications of NMR spectroscopy?
6. Explain the Selection rules of NMR spectroscopy.
7. Define Chemical shift.
8. Explain Shielding and Deshielding effect of NMR spectroscopy.
9. Define the term Chromophore with example.
10. Explain different possible electronic transitions in UV-Spectroscopy of Carbonyl compound.

## ***Descriptive Questions:***

1. Describe the principle, instrument and applications of electronic spectroscopy (UV).
2. Describe the principle, instrument and applications of IR spectroscopy.
3. Describe the principle, instrument and applications of NMR spectroscopy.

UNIT-V

4. Write about Electromagnetic spectrum (Wavelength and Frequency chart).
  5. Write about the principle and applications of Magnetic Resonance Imaging (MRI).

### *Objective Questions:*

***Fill in the blanks:***

1. Another name of the Ultra violet spectroscopy is **Electronic spectroscopy**.
2. According laporte selection rule **g-u** and **u-g** are the allowed transitions.
3. **Tungsten lamp (or) H<sub>2</sub>-lamp (or) D<sub>2</sub>-lamp** is the source of UV spectroscopy.
4. **200 -400 nm** is the wavelength range of the UV spectroscopy.
5. **1446-600 Cm<sup>-1</sup>** is the finger print region in the IR spectroscopy.
6. **Nernest filament (or) Glober(or) hot quartz** is the source of IR spectroscopy.
7. **Nuclear Magnetic Resonance** is the full form of NMR spectroscopy.
8. **60 and 800 MHz** is the radio frequency (RF) range in NMR spectroscopy.
9. Chemical shift in NMR spectroscopy is expressed with **δ** symbol.
10. **TMS(tetra methyl silane)** is used in NMR as reference solvent.