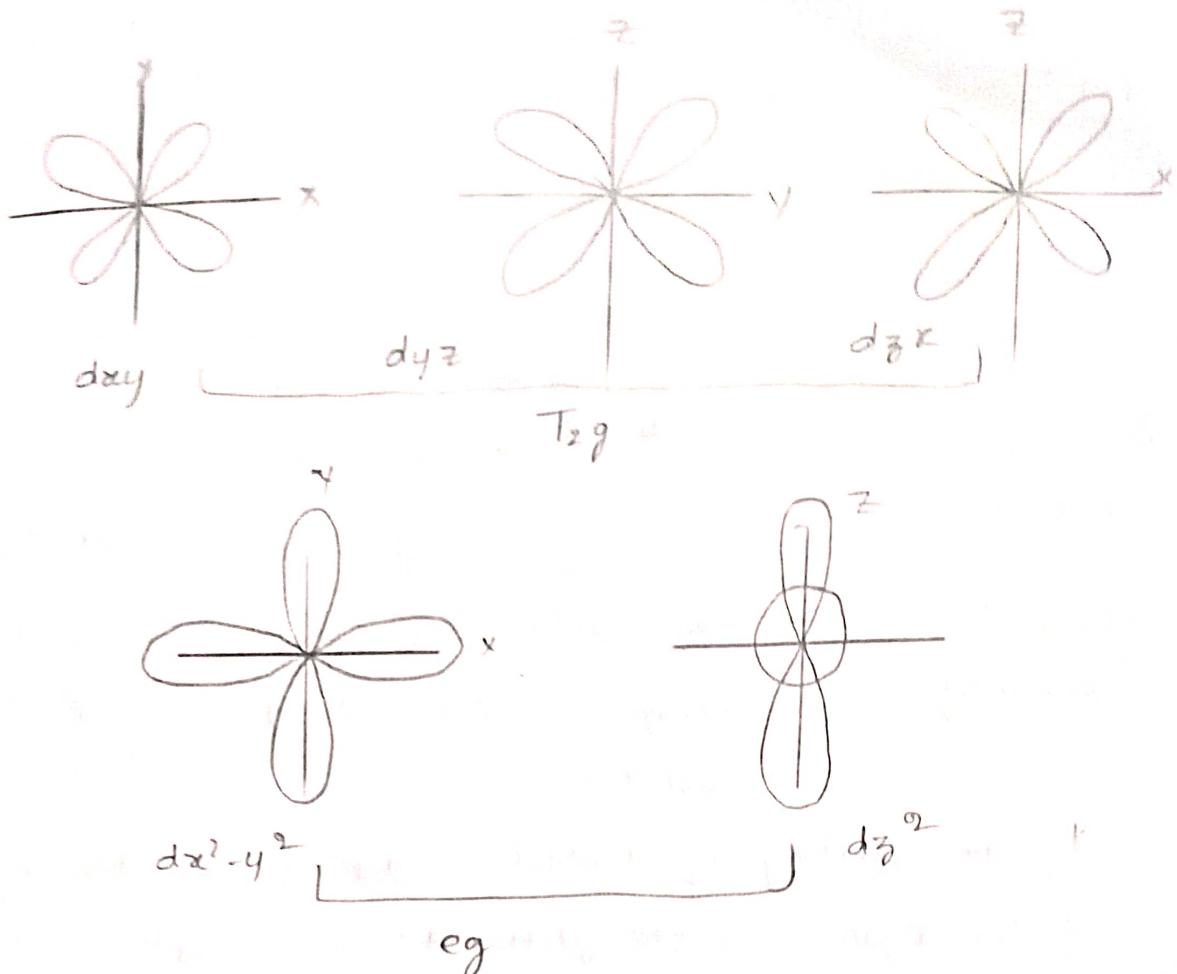


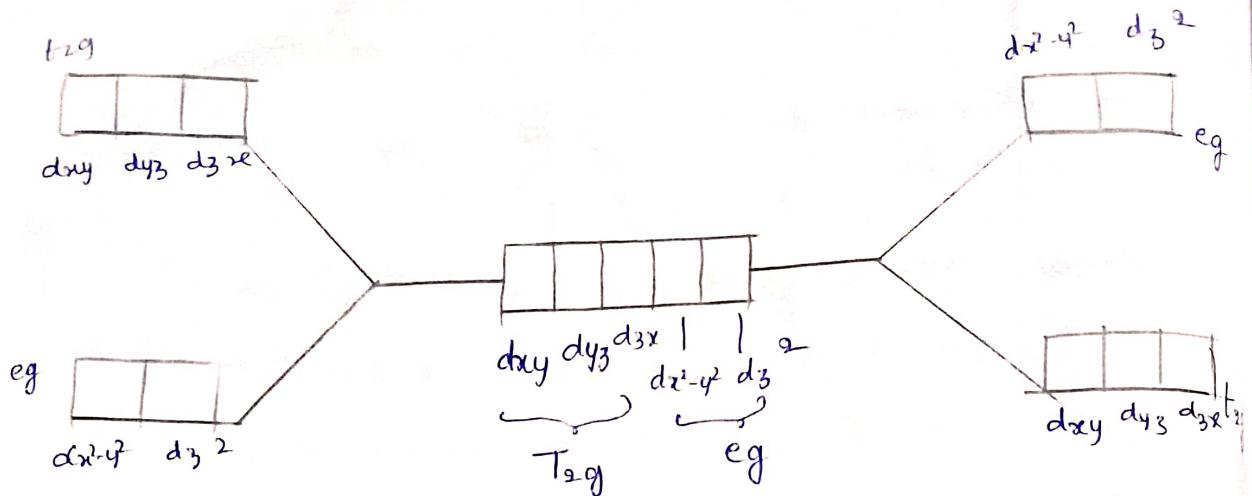
## UNIT-II

### Salient features of crystal field Theory

- \* It is mainly applicable for transitional metal complex.  
Eg :- Sc, Ti, V, Cr, Mn, Fe, etc
- \* According to this theory the central metal ion of the complex is carried as point charge, similarly ligands or molecules or ions also carried as point charges.
- \* The central metal ion (+ve charge) and the surrounding ligands (-ve / Neutral charge) are assumed to be ionic.
- \* The Electrostatic forces of attraction between central metal atom or ion and surrounding ligands or molecules or ions
- \* The metal consists of 5-d orbitals i.e  $d_{xy}$ ,  $d_{yz}$ ,  $d_{zx}$ ,  $d_{z^2}$ ,  $d_{x^2-y^2}$  orbitals
- \* The ligands (-ve charge towards the central atom if it is symmetrically charge distribution resulting the 5-d orbitals exhibit degeneracy on same energy levels)
- \* The (-ve charge around the central atom if unsymmetrically distributed - the degeneracy of orbitals disappeared (i.e splitting of d-orbitals))
- \* The  $T_{2g}$  Orbitals are probability of electron density in between the axis and ~~away from~~ eg orbitals of the probability of electron density along the axis



- \* In octahedral geometry eg orbitals occupy highest energy (due to repulsions between metal and ligand electrostatic forces high) and  $T_{2g}$  orbitals are occupying lowest energy (due to less repulsions between metal and ligand electrostatic forces)
- \* In tetrahedral geometry easy orbitals are occupying lowest energy (due to less repulsions between metal and ligand electrostatic forces) and  $T_{2g}$  orbitals are occupying highest energy (due to repulsions between metal and ligand electrostatic forces)

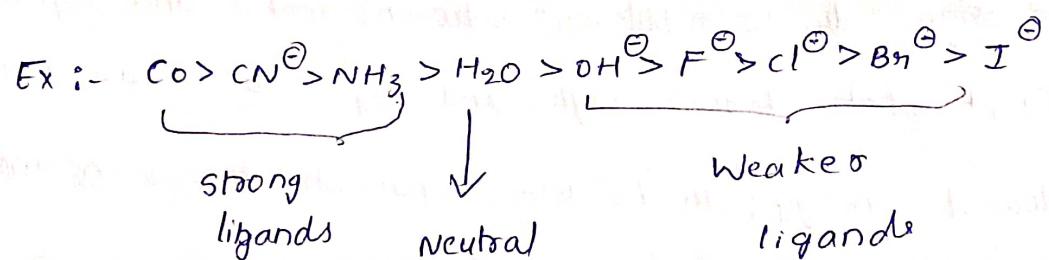


tetrahedral  
geometry

all orbitals are equal  
energies for degeneracy  
orbital

Octahedral  
geometry

- \* The splitting of d-orbitals depends on the ligands if the ligands are strong, the d-orbitals split strongly and ligands are weaker the d-orbitals split weakly or less.



- \* If ligands are strong fields the electrons from metal occupies lowest energy levels (follow Hund's rule) resulting it exhibits less no. of unpaired e<sup>-</sup>. Hence these complexes are low spin or spin-paired complexes.
- \* If ligands are weak the electrons from metal occupy all the d-orbitals (doesn't follow Hund's rule) resulting it exhibits more no. of unpaired e<sup>-</sup>. Hence these complexes are known as high spin (or) spin free complexes.

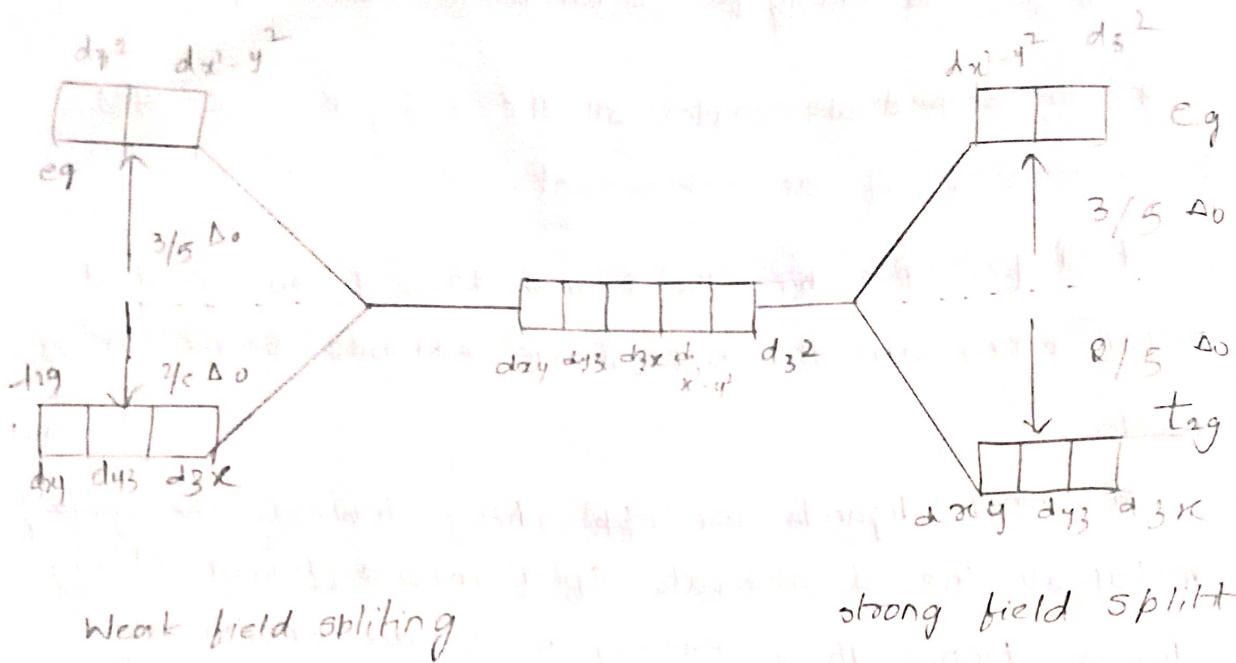
## Crystal Field theory for Octahedral Geometry

- \* In octahedral complex all the 6 ligands occupy the 6 corners of an octahedron.
- \* Before approaching the ligands towards the central metal atom all the 5 d-orbitals exhibits same energy levels.
- \* When ligands are approaching towards the central metal, all the d-orbitals split into different energy levels. Hence these energy levels are known as Crystal Field splitting energy levels.
- \* If ligands are approaching along the axis there is a repulsions between metal eg orbitals and ligand electrons resulting eg orbitals are occupying highest energy when compared with t<sub>2g</sub> orbitals (due to less repulsions b/w t<sub>2g</sub> orbitals and ligand electrons).
- \* The difference b/w the eg and t<sub>2g</sub> orbitals are designated  $\Delta_0$  (Subscription of 0 represents the octahedral Geometry) Hence the difference of these energy levels are known as crystal field stabilization energy levels (CFSE).
- \* The eg orbitals raised  $\frac{3}{5} \Delta_0$  (or) 0.6  $\Delta_0$  and t<sub>2g</sub> orbital are  $\frac{2}{5} \Delta_0$  (or) 0.4  $\Delta_0$  energy levels from degeneracy of d-orbitals.

$$\Delta_0 = 0.4 \times t_{2g} - 0.6 \times e_g$$

t<sub>2g</sub> - No. of e<sup>-</sup> present with t<sub>2g</sub> orbitals

e<sub>g</sub> - No. of e<sup>-</sup> present with e<sub>g</sub> orbitals



Ex:- CFT for HexacyanoIron(II) Complex  $[\text{Fe(CN)}_6]^{2+}$

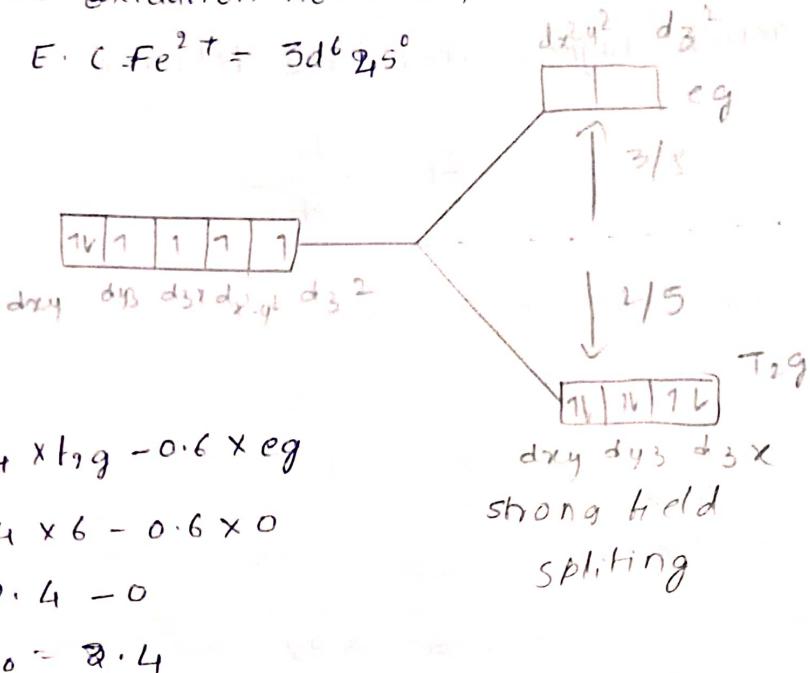
- \* Hexacyanoferron(II) complex exhibit octahedral geometry
- \* The above complex, iron is the central metal ion and 6 CN ligands are considered as strong field ligands
- \* All the ligands towards the iron ion occupying octahedral nature.
- \* Before approaching the ligands towards the central metal ion all the d-orbitals exhibit same energy levels.
- \* If ligands are approaching towards the central metal ion along the axis resulting eg orbitals are occupying highest energy (due to more repulsions between eg orbitals and ligand electrons) and t<sub>2g</sub> orbitals occupying lowest energy (due to less repulsion between t<sub>2g</sub> orbitals and ligand electrons)

\* eg orbitals exhibits  $3/5 \Delta_o$  and  $T_{2g}$  orbitals  
are exhibits  $2/5 \Delta_o$ .

atomic number of Fe = 26  
 $E.C.Fe = 3d^6 4s^2$

Fe oxidation no. = 2+

$E.C.Fe^{2+} = 3d^6 4s^0$



$$\begin{aligned}\Delta_o &= 0.4 \times t_{2g} - 0.6 \times e_g \\ &= 0.4 \times 6 - 0.6 \times 0 \\ &= 2.4 - 0 \\ \Delta_o &= 2.4\end{aligned}$$

$d_{xy} \ d_{yz} \ d_{zx}$   
 strong field  
 splitting

Crystal Field theory for tetrahedral complex (at):-

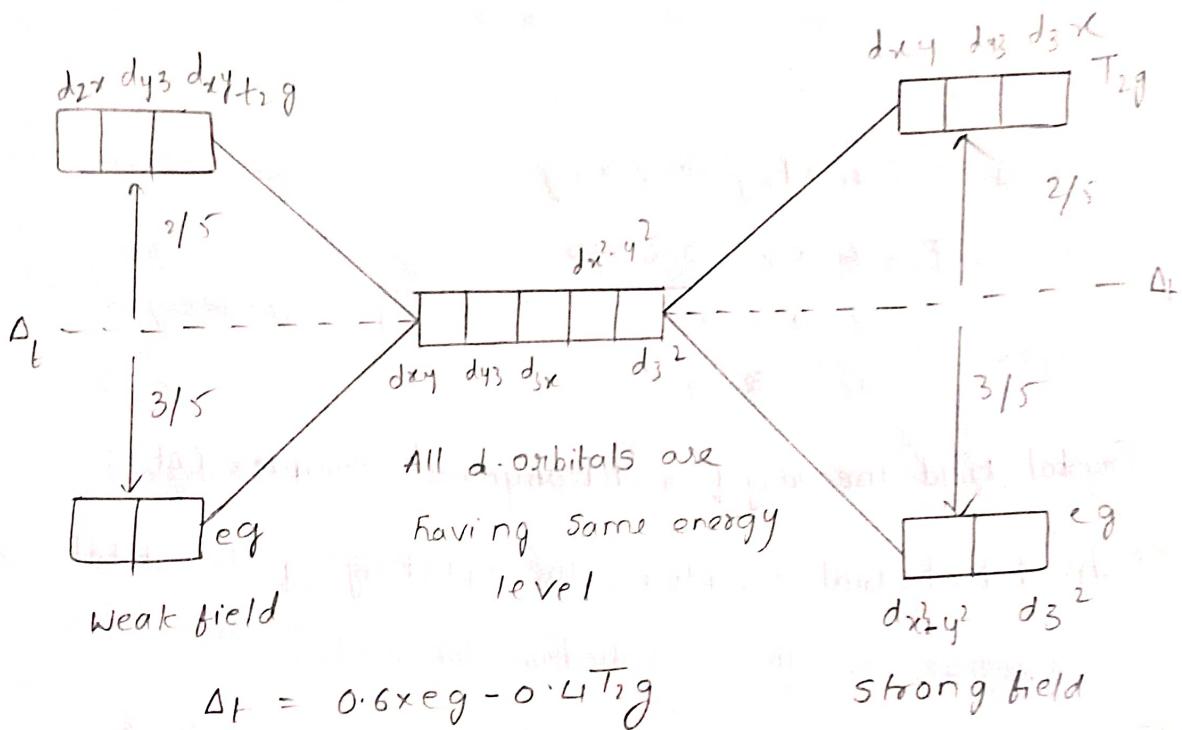
- ⇒ In tetrahedral complex, the splitting of d-orbitals is reverse to the octahedral Geometry
- ⇒ In tetrahedral complex, the four ligands are approaching towards the central metal ion (or) in between the axis.
- ⇒ Before approaching the ligands towards the central metal ion all the d-orbitals exhibit same energy levels.
- ⇒ When ligands are approaching towards the central metal ion "T<sub>2g</sub>" orbitals occupy highest energy levels when compared with "e<sub>g</sub>" orbitals. Due to less

repulsion between "eg" orbitals and ligand electrons

⇒ The crystal field splitting of tetrahedral complex are represented with  $\Delta_t$ .

⇒ The crystal field splitting of octahedral complex much higher than the tetrahedral complexes

$$\Delta_t = \frac{4}{9} \Delta_o$$



### Properties of Co-ordination compounds :-

#### ① Magnetic Property

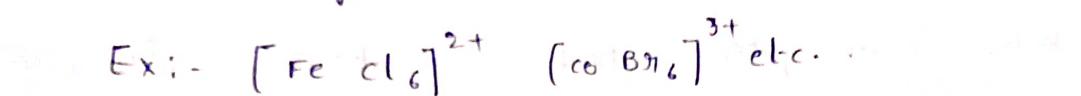
⇒ Inner orbitals or low spin or spin paired complex are those complexes in which hybrid orbitals are formed by hybridization of  $(n-1)d$  orbitals exhibit diamagnetic in nature.

⇒ outer orbitals or high spin or spin free complexes are those complex in which hybrid orbitals are formed by hybridization of ns, np and nd orbitals exhibit paramagnetic in nature.

⇒ The substances having no unpaired electrons show 0 magnetic or diamagnetic in nature.



⇒ The substances which are having unpaired electrons exhibit paramagnetic in nature.



⇒ The magnetic momentum  $\mu = \sqrt{n(n+1)}$  where n is equal to no. of unpaired electrons.

$$\text{Ex :- If } n=1 \quad \mu = \sqrt{1(1+1)} = 1.78$$

$$n=2 \quad \mu = \sqrt{2(2+1)} = 2.83$$

⇒

## ② Colour property

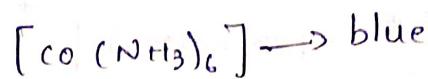
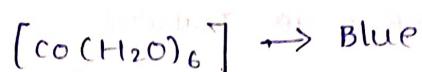
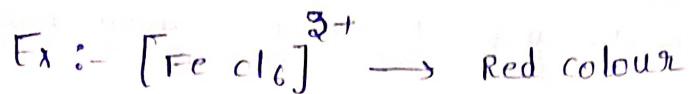
⇒ Crystal Field Theory can explain the colour properties of transitional metal complexes.

⇒ According to this Theory the electrons are transferred from lowest energy orbitals [T<sub>2g</sub>] to higher energy orbitals [e<sub>g</sub>]

⇒ If the substance which has absence of ligands crystal field splitting does not takes place. Hence the substance is always colourless.

⇒ If the substance which has ligands so crystal

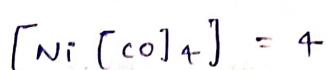
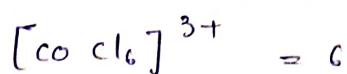
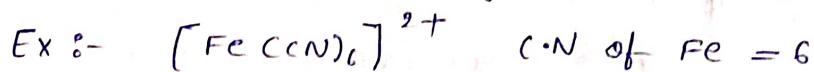
field splitting takes place. Hence the substance are coloured in nature.



### ③ Co-ordination number

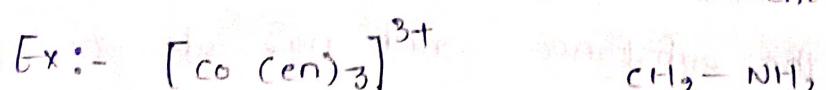
→ It is defined as the number of molecules or ions bound with central metal atom or ion with specific geometry is known as co-ordination number.

→ If ligands are mono dentate ligands the co-ordination number is equal to the ligands number.

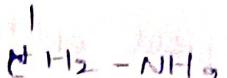


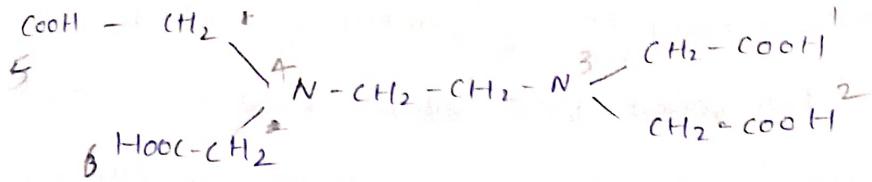
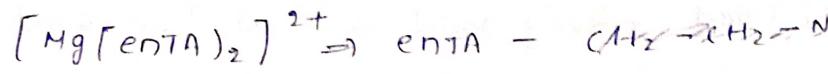
→ If ligands are poly dentate the co-ordination number is equal to the no. of ligands multiplied with bonding sides [dentity].

$$\text{Co-ordination number} = \text{no. of ligands} \times \text{dentity}$$

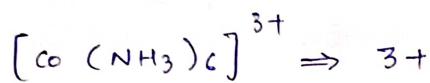
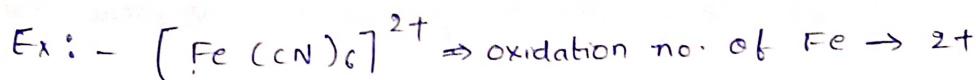


$$\begin{aligned} \text{C.N} &= 3 \times 2 \\ &= 6 \end{aligned}$$





④ Oxidation state :- The charge of the complex if all the ligands are removed along with the electron pairs that are shared with the central metal atom or ion is called oxidation number of the central metal atom or ion

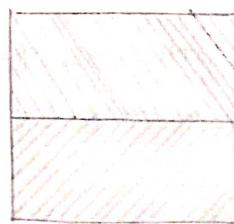


#### \* Band diagrams for solids

**Conductors:** If a solid is conductor it has either partially filled or completely filled Valency band to conduction band electrons are easily transferred. Hence, they called as Conductors. ~~and~~ due to overlapping of Valency band and Conduction band for this solids there is no forbidden gap between Valency band and conduction band. The electrical conductivity of conductors decreases with increasing the temperature due to scattering of the electrons.

Ex:- Cu, Al, Fe, Ag etc

Band structure for conductors

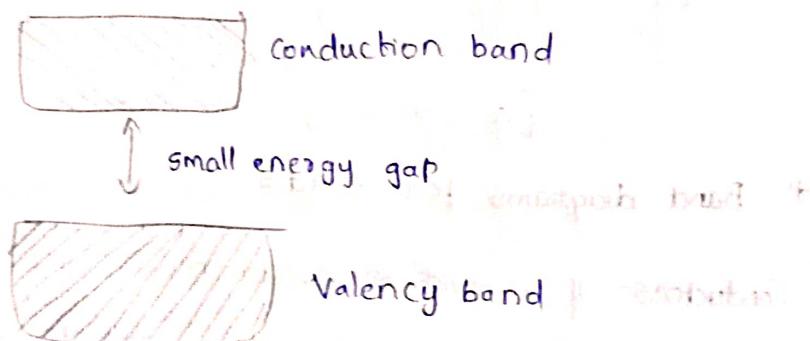


Conduction Band

Valence Band

**Semiconductors:** If a solid is semiconductor it has completely filled Valency band to conduction band has very narrow (small) energy gap Hence there is no electrons transferred from Valency band to conduction band at room temperature hence these substances are known as Semiconductors. These semiconductors conductivity increases with increasing the temp due to some electrons are transferred from valency band to conduction band.

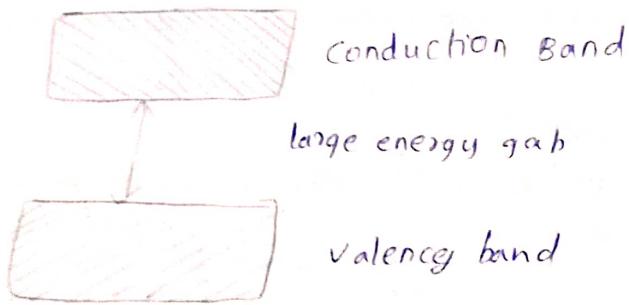
Ex:- Boron, silicon, germanium, arsenic, antimony



Band structure for Semiconductors

**Insulators:** If a solid is an insulator the energy gap between Valency band and conduction band is large Hence a completely filled Valency band to conduction band electrons does not allow even at room temperature are at higher temperature. Hence the solids are called as insulators if the solid substances heat at higher temperature ( $1000^{\circ}\text{C}$  to  $20,000^{\circ}\text{C}$ ) the electrons allow Valency band to conduction band. Hence they acts as a conductor

Ex: Diamond, Glass  
( $60\text{eV}$ ) ( $10\text{eV}$ )



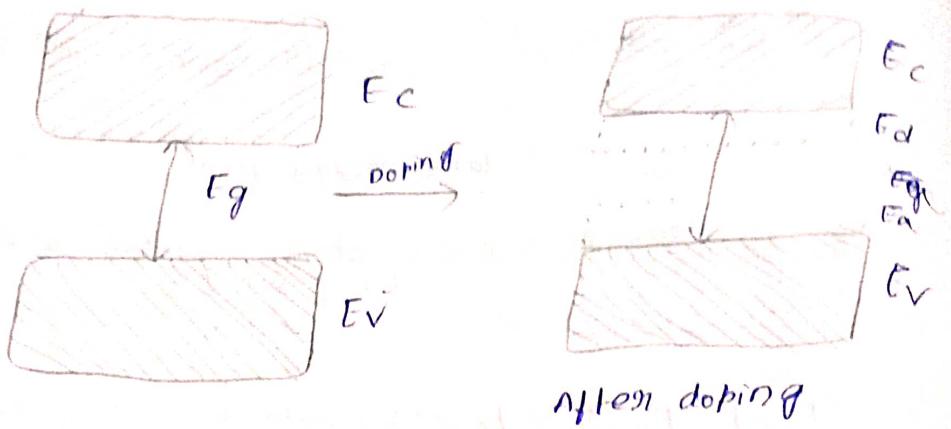
Band structure for Insulators

### Effect of doping on band structures

- \* The process of incorporating the desired type of impurities in a crystal lattice is called Doping \*
- \* The conducting properties have been improved by adding small amount of impurity is called doping agents or dopants.
- \* All extrinsic semiconductors are basically intrinsic semiconductors.
- \* The addition of doping agent reduces the energy gap between valency band and conduction band hence it allows the electrons from valency band to conduction band.
- \* The energy gap between valency band and conduction band are known as intrinsic Energy gap.

$$Eg = E_C - E_V \quad E_C - \text{energy (gap) of} \\ \text{Conduction band}$$

- \* usually 1 part of doping agent is added to  $10^6$  parts the semiconducting materials it causes the impurity atoms exhibits energy levels in between the valency band and conduction band.



Band structure for semiconductors

Where  $E_C$  = Energy of conduction Band

$E_V$  = Energy of valency band

$E_D$  = Energy of donor atoms

$E_A$  = Energy of acceptor atoms

### Super Capacitors :-

- \* Super capacitors are normally used as energy storage devices.
- \* Super capacitors store large amount of electric charge compared to the electrolytic capacitors and all other types of conventional capacitors.
- \* The super capacitors consists of large surface area electrodes and very thin dielectric which makes it possible to achieve very large capacitance.
- \* Super capacitors normally store 10 to 100 times more charge per unit volume than electrolytic capacitors.

### Supercapacitor definition :

Supercapacitor is an electronic device that stores large amount of electric charge or electric energy.

These capacitors are also known as ultracapacitors or electric double layer capacitors.

### Types of Supercapacitors

They are classified into different categories:

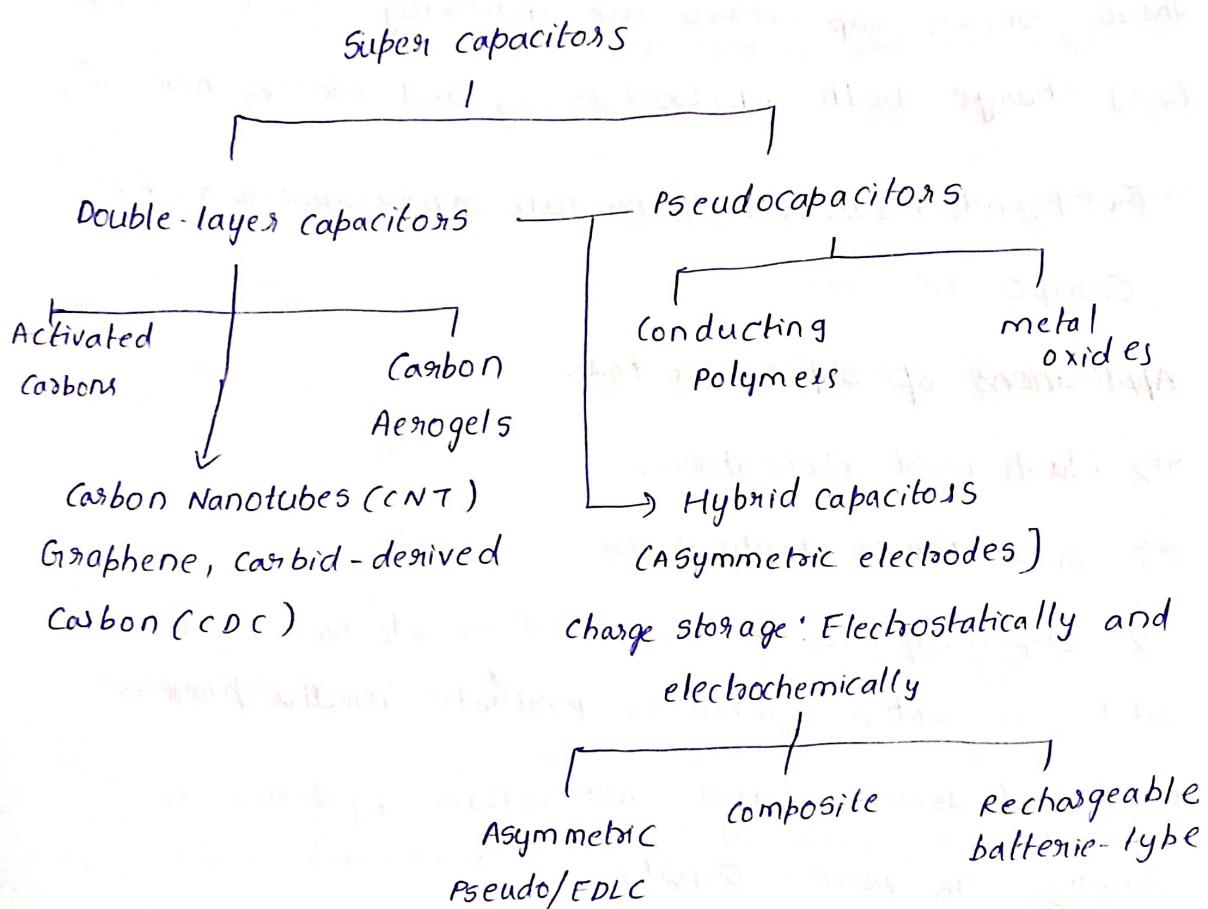
\* Classification according to different energy storage mechanism

⇒ Electric double layer capacitor (EDLC)

⇒ Pseudo capacitors

⇒ Hybrid capacitors

classification according to different energy storage mechanisms.



### Electrical double layer capacitors (EDLC):

⇒ These are known as symmetrical supercapacitors.

\* These capacitors energy (or) charge can store electrostatically

Ex:- Carbon aerogel, carbon derived carbon (CDC)

## Graphene and Activated carbon.

### Pseudo-Capacitors:

These are known as asymmetrical Supercapacitor.  
These capacitors stores energy (or) charge electro-chemically.

Ex: Conducting polymers, Metal oxides etc.

### Hybrid Capacitors:

These are combination of Electrical double layers and Pseudo capacitors.

These super capacitors are generally store energy (or) charge both electrostatically and electrochemically

Ex: Pseudo + EDLC, Lithium ion supercapacitors (LISC), Composite etc.

### Applications of Supercapacitors.

- ⇒ Flash light applications.
- ⇒ Solar power applications.
- ⇒ Supercapacitors are used in electronic devices such as laptop computers, portable media players, hand held devices, and photovoltaic systems to stabilize the power supply.
- ⇒ Supercapacitors are used as temporary energy storage devices for energy harvesting systems.
- ⇒ Supercapacitors are used in defibrillators (an

Instrument that controls irregular heart beat by supplying electric current to the chest wall).

⇒ Used as backup energy source for GPS guided missiles.

⇒ Used in public transportation

Ex: Japan, Hong Kong, China, South Korea.

⇒ Hybrid electric vehicles to start and stop systems.

⇒ Supercapacitors provide backup or emergency shutdown power to low-power equipment

Ex: UPS etc

⇒ They used in industrial lasers and medical equipment

⇒ Large supercapacitors are used in wind turbines

⇒ Used as voltage stabilizers.

⇒ Used in diesel engine in submarines & tanks.

### Nano Materials

\* Nano chemistry is a new discipline concerned with unique properties and associated with arrangement of atoms/molecules on a nano scale range (between 1-100 nanometers) between that of individual building blocks.

- The term "Nano" stands for one billion of a meter in a physical scale length.
- Nano chemistry is defined as the study of synthesis and analysis of materials in nano scale range (1-100 nanometers) including large organic molecules, inorganic

cluster compounds and metallic (or) Semiconductor particles.

Definition:

- ⇒ Nano Material's are materials with dimensions and tolerances in the range of 0.1 - 100 nm. They can be metals, ceramics, polymeric materials or composite materials.
- ⇒ Nano materials are biological, inorganic (or) organic (substances) structures that, due to their small size, exhibit unique properties different from those observed in bulk materials.
- ⇒ Nano material's play an important role in the different in shape, composition, size, surface structure with optical target and controls self assembly of their building blocks at different scale lengths.
- ⇒ The average sizes of commonly known things in nanometer are tabulated below.

	Size (nm)	
BuckyBall	1	nano
Carbon nanotube (diameter)	10 <sup>-3</sup>	
DNA	2	
E. coli bacteria	2000	Micro
Human eye can see	10,000	
Human hair (diameter)	25,000	

Ant	5 million	Macro
Apple	80 million	

## Classification of nanomaterials.

Nanomaterials generally classified on the

- Basic of atoms/molecules array and
- Pore dimensions

Based on atoms/molecules array nanomaterials are classified into three types.

\* Materials with one dimension in the Nano scale

Ex :- thin films, surface coatings

\* Materials with two dimension in the Nano scale

Ex : Nanowires, Nanotubes, nanofibers, biopolymers etc.

\* Materials with three dimension in Nano scale

Ex : Fullerenes, nano particles, dendrimers etc.

## Classification based on pore dimensions

Nanoporous materials are classified in three main groups depending on their pore dimension:

Microporous materials ( $d < 2\text{ nm}$ ):

- These materials have very narrow pores
- They can host only small molecules, such as gases or linear molecules.
- Generally show slow diffusion kinetics and high interaction properties.
- They are generally used in gas purification systems, membrane filters or gas-storage materials.

Ex: Na-Y and naturally occurring clay materials

Mesoporous materials ( $2 < d < 50 \text{ nm}$ ):

- These materials have pores with diameter size enough to host some big molecules, for example aromatic systems or large polymeric monomers.
- Moderate diffusion of the adsorbed molecules is often due to capillarity, with an initial interaction with the pore wall followed by pore filling.
- These systems can be used as nano-reactors, the polymerization or adsorbing systems for liquids or vapours.

Ex: MCM-41, MCM 48, SBA 15 and Carbon mesoporous materials etc.

Macroporous systems ( $d > 50 \text{ nm}$ ):

- Pores of these materials could host very large molecules such as poly-aromatic systems or small biological molecules.
- Interactions with pore walls are often secondary respect to the interactions with other molecules, overwall in the case of very small guest molecules.
- These materials are principally used as matrices to functional molecules, as scaffolds to graft functional groups, such as catalytic centres and as sensing materials.
- The quick diffusion of chemical species in pore system

Ex: Carbon micro tubes, porous gels and porous glasses.

## Fullerenes

### Introduction:

- ⇒ A fullerenes is an allotrope of Carbon.
- ⇒ It is in the form of a hollow sphere, ellipsoid or tube and many other shapes.
- ⇒ The structure of fullerenes is similar to Graphite.  
⇒ ~~the first form~~ It consists of spherical fullerenes called bucky balls, resembles the foot ball.
- ⇒ It consists of hexagonal rings and alternate pentagonal rings of carbon closed in different forms.
- ⇒ The second form of cylindrical fullerenes are also called Carbon nanotubes or bucky tubes.

### Properties of fullerenes:

1. Stability: Fullerenes are stable molecules.
2. Hybridization: The hybridization of carbon atoms in fullerenes lies in between  $sp^2$  and  $sp^3$ .
3. Chemical properties: Fullerenes are mainly involved in electrophilic addition reactions.
4. Solubility: Fullerenes are sparingly soluble in many solvents but soluble in toluene and  $CS_2$ .
5. Color: Fullerene ( $C_{60}$ ) is fine black powder, solutions of pure Buckminster fullerene have a deep purple color.

Solutions and solutions of C<sub>60</sub> are a reddish brown color.

Conductivity: Fullerenes are available electrical insulators as there is no movement of electrons available from one carbon to another carbon.

Hydrogenation: As C<sub>60</sub> exhibits a small degree of aromatic character, it undergoes addition reaction with hydrogen.

Halogenations: C<sub>60</sub> undergoes halogenations with F<sub>2</sub>, Br under verify of conditions.

They possess cage like structure

They possess excellent tensile strength

They possess high packing density

Applications of fullerenes.

1. Fullerenes are used as good antioxidants, so it finds application in health and personal care.
2. Bucky balls are very good medium to make hydrogen fuel.
3. Fullerenes nano tube is used in as tips in scanning probe microscopy (SPM).
4. It inhibits HIV virus.
5. fullerenes act as catalyst in some organic reactions.
6. It is used in water purification.
7. It is used in fuel cell membrane materials.

8. C<sub>60</sub> Buckyballs can be used as traces in human body.
9. Fullerenes blended with polymers are used as in organic photovoltaic's.
10. It is used as a coating material on chemical sensors.
11. It is used as filters.
12. It is used as drug delivery.

### Carbon Nanotubes (CNTs)

- \* Carbon nanotubes is a tubular form of carbon with 1-3nm diameter and a length of few nm to microns.
- \* Generally carbon in the solid phase exists in different allotopic forms like graphite, diamond, fullerenes and nano tubes.
- \* Carbon nanotubes are tubular forms of carbon.
- \* When graphite sheets are rolled into a cylinder, their edges join to each other form carbon nanotubes.
- \* Each carbon atom in the carbon nanotubes is linked by covalent bonds.
- \* The number of nanotubes align into tubes and are held together by weak van der walls forces.

### Properties of CNTs

- They possess remarkable tensile strength.
- They can be insulators, semiconductors and conductors depending on the way graphite structure spirals around the tube.
- They possess large surface area.
- They show good properties in electron emission.

- They are thermally stable in a vacuum upto  $2800^{\circ}\text{C}$
- They exhibit excellent electric power properties (1000 times better than copper wires).
- They exhibit good mechanical properties.
- They possess electric elastic and flexibility.
- The atoms in nanotube are continuously vibrating back and forth.
- It is highly conducting property and behave like metallic conductor and semiconductors.
- It has highly thermal conductivity.
- It has good kinetic properties.

### Applications of CNTs

- It is used in battery technology and also used as cathode.
- CNTs are used effectively for drug delivery application.
- It is used in light weight shielding materials for protecting electric equipment.
- It is used in composites and ICs.
- It also act as catalyst for some chemical reaction.
- It acts as a very good biosensor, Due to chemical inertness carbon nanotubes are used detect many molecules present in the blood.
- It is also used for softening process as filter.
- It is used in polymers LED.
- It is used in electrical energy storage application.
- It is used in ultra-resistant materials for use as reinforcement fibers.

## Graphene's

- ⇒ Graphene is the name for an atom-thick honeycomb sheet of carbon atoms.
- ⇒ It is the building block for other graphitic materials (since a typical carbon atom has a diameter of about 0.33 nanometers, there are about 3 million layers of graphene in 1mm of graphite)
- ⇒ Units of graphene are known as nanographene.
- ⇒ Nanographene is made by selectively removing hydrogen atoms from organic molecules of carbon and hydrogen, a process is called dehydrogenation.

## Graphene properties

- \* They possess good electronic properties.
- \* They possess good electrical conducting properties.
- \* They possess good mechanical properties.
- \* They are light in weight, rigid and more stronger than steel.
- \* They possess good thermal conductor.
- \* They are crystalline and allotrope of carbon.
- \* Graphenes are chemically more reactive.
- \* They possess good thermal stability
- \* They possess good optical nature.

## Graphene applications

- ↳ It is used in Energy storage and solar cells.
- ↳ It is used in sensor applications.
- ↳ It is used as graphene links in electronics and electrical

- ↪ It is used in transistors and memory storage devices
- ↪ It is used in flexible, stretchable and foldable electronics
- ↪ It is used in photodetectors.
- ↪ It is used in surface coating for corrosion.
- ↪ It is used in loudspeakers.
- ↪ It is used in biotechnology and medicine.
- ↪ It is used in radiation shielding.
- ↪ It is used in cloaking.
- ↪ It is used in lubrication.
- ↪ It is used in water purification.
- ↪ It is used in face masks.