

UNIT-II

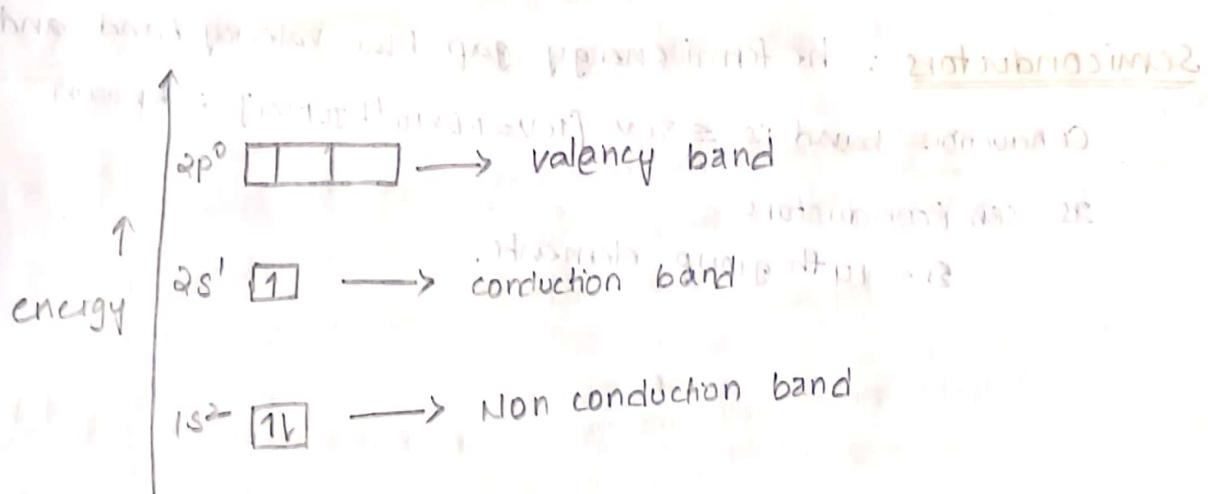
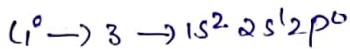
G1a.2 Discuss about modern engineering materials.

MODERN ENGINEERING MATERIALS

Band theory of solids :

Felix Bloch proposed band theory of solids to explain conductors, semiconductors and insulators in 1928.

Conductors, semiconductors and insulators in 1928.
In our periodic table lithium is first solid state element



Non conduction band

The completely filled orbitals produce non conduction band in lithium element. $1s^2$ Orbital produce non conduction band.

Conduction band :- the partially filled orbitals produce conduction band

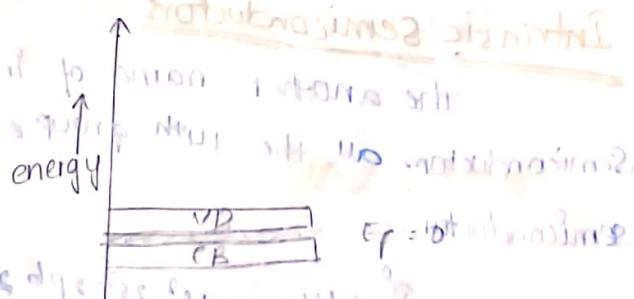
band in lithium element. $2s^1$ orbital produce conduction band

Valency band :- the empty orbitals present in valency level produce valency band. In lithium element $2p^0$ is vacant orbital

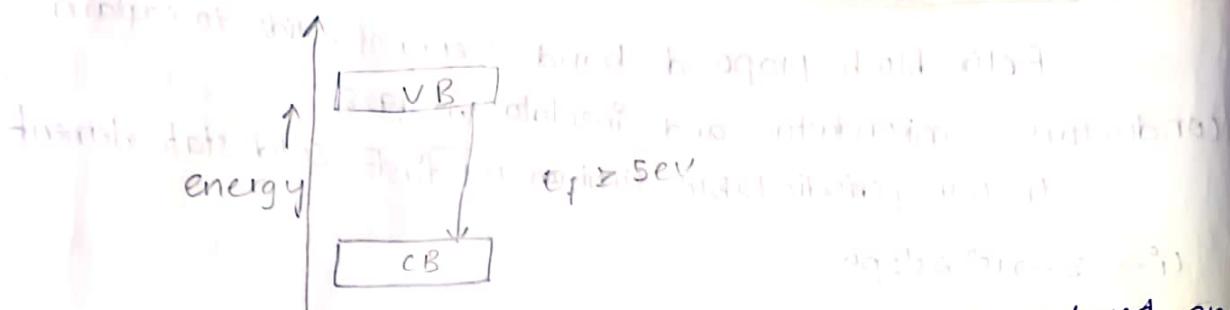
produce valency band.

Conductors :- the fermi energy gap b/w valency band and conduction band is '0' that means both bands are overlapped.

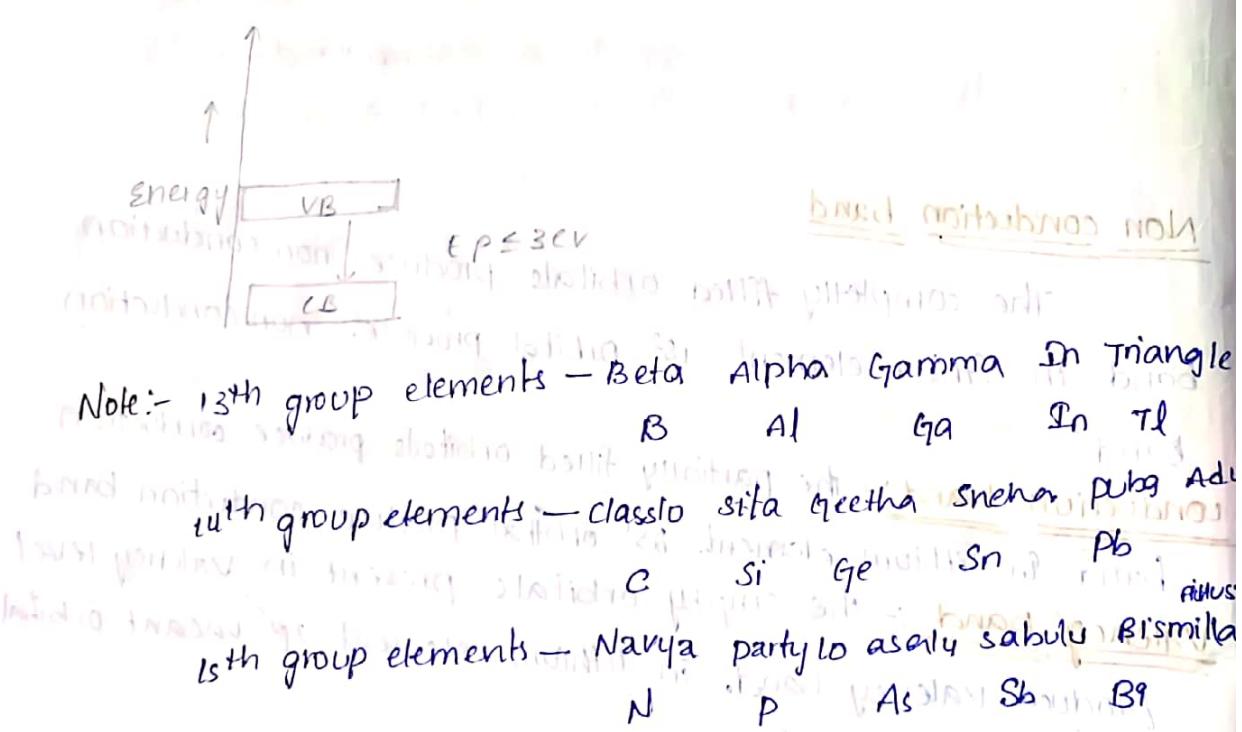
Ex: all metals.



Insulators: The fermi energy gap between valency band and conduction band is $\geq 5\text{eV}$ [$1\text{eV} = 1.6 \times 10^{-19}$ Joules] is known as Insulators.
Ex: nonmetals, plastic, wood, paper etc.

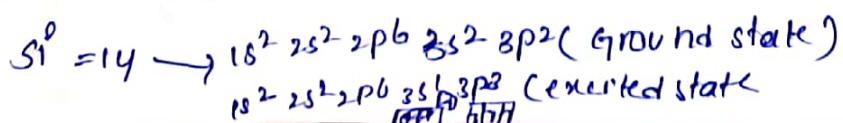


Semiconductors: the fermi energy gap b/w valency band and conduction band is $\leq 3\text{eV}$ [$1\text{eV} = 1.6 \times 10^{-19}$ Joules] is known as semiconductors.
Ex- 14th group elements.



Types of Semiconductors

Intrinsic Semiconductors
 the another name of Intrinsic semiconductors is pure Semiconductor. all the 14th group elements acts as (Pn) Intrinsic semiconductor.



Extrinsic Semiconductor.

On the basis upon addition of impurities extrinsic semiconductors are divided into 2 types those are i. p-type semiconductors or p-doped Semiconductors.

P type Semiconductors:- the addition of 13th group elements has a semiconductor.

Here 13th group elements have three valency electrons but our requirement is 4 electrons, so that 4th valency should be balanced by positively charged hole.

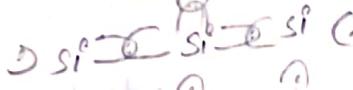
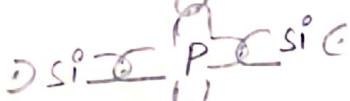
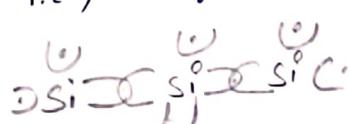
Impurities are 14th group elements.

Impurities are 13th group elements.

holes are majority carriers and holes are minority carriers.

n type semiconductor:- the addition of 15th group element has a 5 valency electrons.

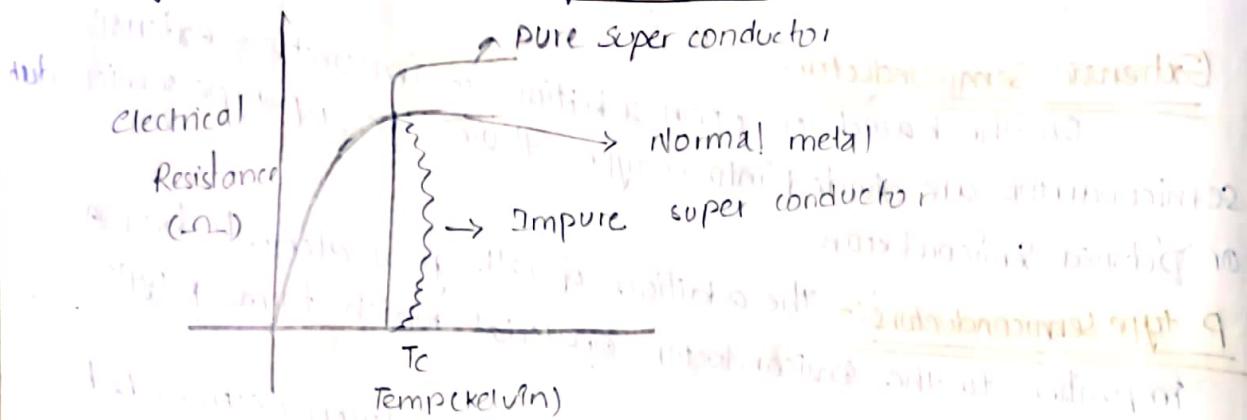
Here 15th group elements have 5 valency electrons but our requirement is 4 electrons so we have one excess electron i.e., surplus electron moves entire the semiconductors.



Superconductors :

A Dutch physicist kamerling onnes proposed super conductor in 1911.

A solid which offers no resistance to passage of electricity through it is known as "superconductors".



Critical temperature

At which temperature super conductor materials convert into normal metal state is known as "critical temperature".

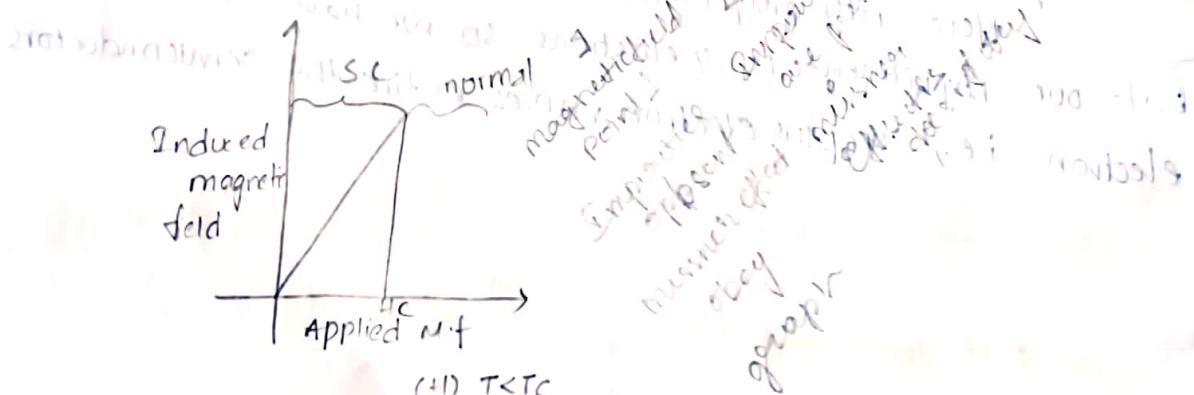
Below the critical temperature that material exhibits super conducting state.

Above the critical temperature that material exhibits normal state of metal.

Classification of superconductors.

Type 1 superconductors :- In type 1 super conductors we have one critical magnetic field, below the critical magnetic field which acts as Super conducting state, above the critical magnetic field which acts as normal metal state. It is also called soft superconductor.

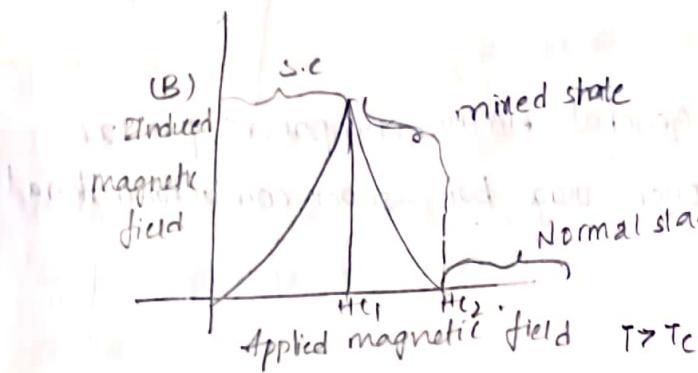
Type 1 superconductor exhibits "meissner effect".



Type 2 super conductors

In type 2 super conductor we have 2 critical magnetic fields (H_{C1} , H_{C2}). Below the H_{C1} that material exhibit super conducting state, in b/w H_{C1} & H_{C2} that material exhibit mixed state, after H_{C2} that material exhibit normal state.

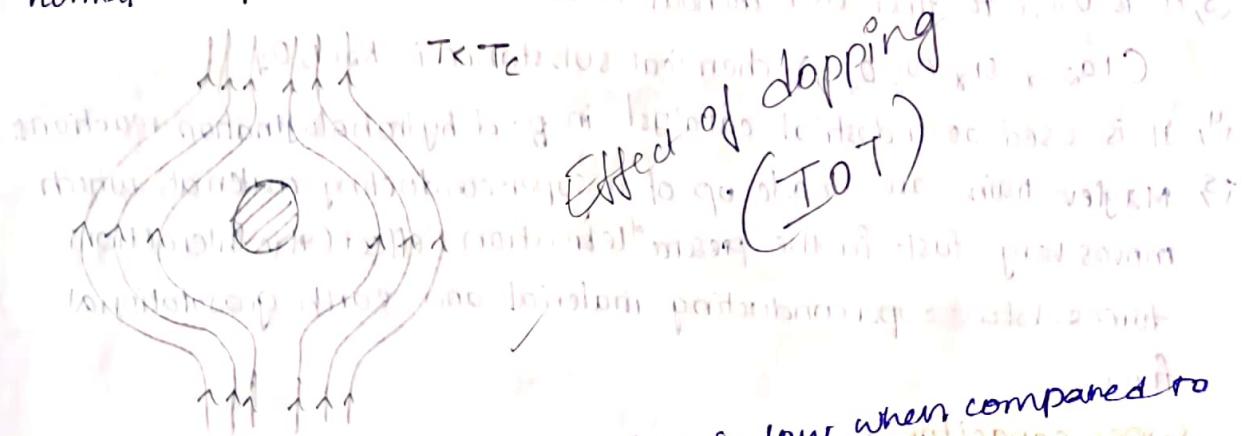
H_{C2} which acts as normal state of metal. It is also known as Hard S.C. Sn type superconductor does not have Meissner effect.



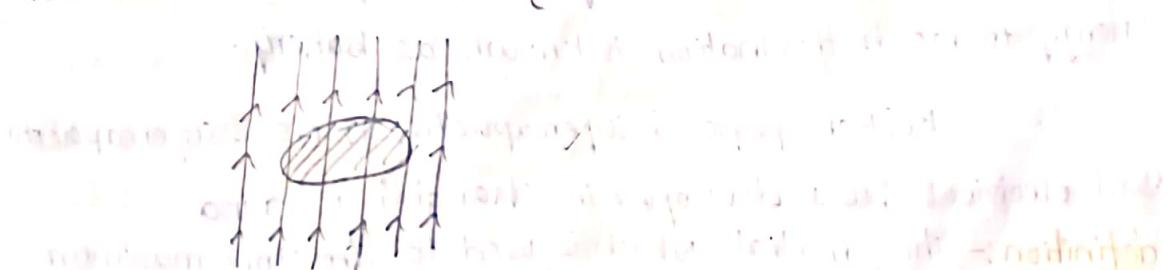
Meissner effect

The complete expulsion of magnetic field by the superconducting material is known as Meissner effect.

1. In case of critical temperature is high when compared to normal temperature ($T < T_c$) which obeys Meissner effect.



2. In case of critical temperature is low when compared to normal temperature ($T > T_c$) which does not obey Meissner effect.



Properties of superconductor:-

- ① Brittle nature - which forms very thin sheets when compared to normal metal.
- ② $I^2 R_D$ (The copper loss equation is always '0' because of input of current is equals to output of current)

3, meissner effect

4, strong magnetic field

5, Diamagnetic nature.

6, Thermoelectric effect - The General electric component produce heat energy to over usage but super conductor material there is no heat energy.

Applications

1, Generally silicon chips are used as storage devices. but we use super conductor chips. These are 1000 times effective than normal silicon chips.

2, Super conductors are used to manufacturing MRI Scanning equipment (Magnetic Resonance Image)

3, It is used to find out alcohol content in drunk and drive cases.

$(La_{2-x}Sr_xCu_3O_{7-x})$ chemical substance is $K_2Cr_2O_7$

4, It is used as industrial catalyst in g. dehydrohalogenation reactions.

5, Maglev trains are made up of a superconducting material which moves very fast in the presence of levitation effect (the interaction forces b/w superconducting material and earth gravitational forces).

Super capacitor

Leyman example: In 200m running race we require more energy to reach destination it is known as super capacitors.

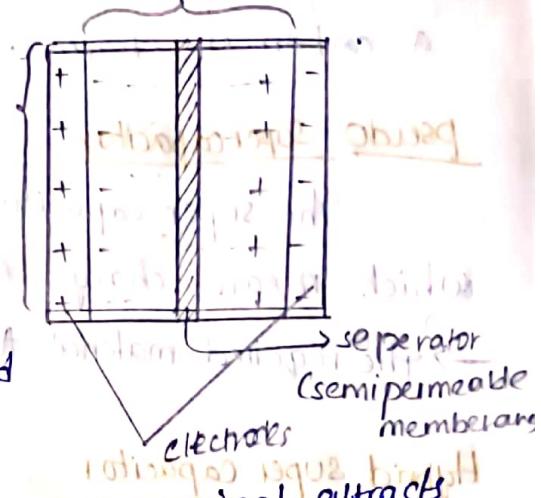
In 20km running race we require less amount of energy to reach destination is known as battery.

Becker proposed supercapacitors in 1997. Supercapacitor used electrical buses developed in shanghai in china

definition: The material which is used to store maximum amount of electrical energy when compared to battery is known as super conductor.

Principle of supercapacitors

In the construction of supercapacitors we take equal length of plates acts as anode and cathode. These plates are separated by semipermeable membrane and electrolyte substance.



- In supercapacitors positive charge cell terminal attracts negatively charged ions from the electrolyte solution which forms one layer.
- In supercapacitors negative cell terminal attracts two positively charged ions from the electrolyte to form another layer.
- The two layers present in supercapacitors which produce some electrode potential which is known as dielectric constant (K-law).

$$C = \frac{\epsilon l}{d}$$

where C = capacitance

ϵ = dielectric constant

l = length of the electrode

d = distance b/w the electrodes.

Classification of super capacitors

on the based upon attraction forces and material taken for electrodes supercapacitors are divided into 3 types those are:

1. Double layer supercapacitor

2. pseudo capacitors

3. Hybrid super capacitors

1. Double layer super capacitors: The supercapacitor undergoes electrostatic forces which means the charge transfer b/w electrodes.

→ The Required electrodes for this super capacitors made up of
a carbon or charcoal powder (CNTs, Graphene)

Pseudo Supercapacitor

The super capacitors which exhibits electrochemical process
which means charge transfer b/w electrode and electrolyte.
→ the required material for the electrodes made up of a ceramics or
conducting polymers)

Hybrid super capacitor :

the supercapacitor which have the properties of double layer and pseudo capacitors is known as hybrid supercapacitors.

the supercapacitors which undergoes electrostatic and electro chemical process.

Properties

- long life
- large storage
- low cost
- more effective

Applications :

- used in laptop computers
- used in preparation of laser medical equipment.
- used in preparation of laser medical equipment.
- 3. These are used in UPS system in Engineering colleges.
- 4. Industrial catalyst.
- 5. It is used in electronic digital switching devices

Nanochemistry

It is a branch of chemistry which deals preparation properties and applications of nanomaterials.

one nanometer is equal to 10^{-9} m = one billionth of meter
In human hair 10000th portion is equals to 1nm
the hydrogen atom size = 0.1nm

Classification

Nanomaterials :- The material which exhibit atleast one dimension b/w one nm to 100nm is known as nanomaterials.

Nanolayer :-

The nano material which exhibits one dimension b/w one nanometer to 100nm is known as nano layer.

Nanotube :-

The nanomaterial which exhibits two dimension b/w one nanometer to 100nm is known as nanotube.

Nanoparticle :-

The nanomaterial which exhibits three dimension b/w 1nm to 100nm. these known as nanoparticles.

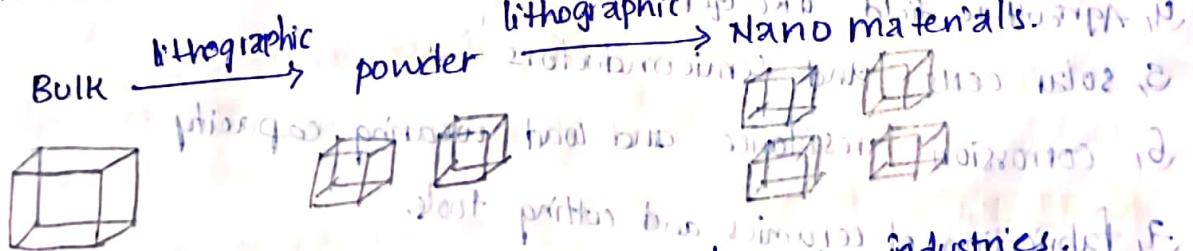
quantum dots :-

The semiconductor material which have one dimension b/w one nm to 100nm is known as Quantum dot.

General methods for preparation of nanomaterials

Topdown approach method

In this method bulk material undergoes lithographic method (stone crushing technique) to form powder further powder undergoes lithographic method to form nano materials.



e.g. This method is used in microelectronic industries.

Bottom up approach method

In this method atoms are aggregated to form clusters. further clusters are aggregated to form nanomaterials.

In this method fullerenes, nanographene, nano particles prepared

Atoms Aggregated clustures Aggregated nanomaterials

→ size → size → size → size

Properties of nanomaterials

- ① Based upon size
 - magnetic property
 - colour
 - solubility, melting point
 - transparency.
- ② composition
 - colloidal → co-existing colloids
 - chemical reactivity
 - Reaction Rate
- ③ Surface
 - conductivity
 - dispersibility
 - catalytic

Applications

- ① electronic and digital switching devices like environmental sensors and LEDs
- ② Industrial catalyst-like cerium oxide (CeO_2), Nickel
- ③ Drug delivery, to control HIV virus
- ④ Agriculture field like Genetic improvement
- ⑤ solar cells and semiconductors
- ⑥ corrosion resistance and load wearing capacity

3, fabrication of ceramics and cutting tools.

Fullerenes: Richard swalley proposed fullerene material in 1985 at Rice University in USA, he awarded noble prize for this concept in 1996. The fullerene name coined by "buckminster fuller"

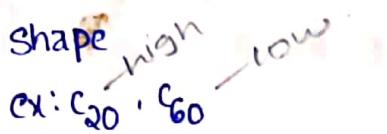
Definition:

"It is an allotrope of carbon element which having ellipsoid, so tube, spherical structure is known as fullerenes."

Classification of fullerene (types)

1, Bucky ball clusters :- this type of fullerenes consists of spherical structures

In ball shape


ex: C_{20} , C_{60}



2, Carbon nano tubes :- this type of fullerenes having hollow tube structures with small dimensions

ex: SWNT's (single wall carbon nano tube)

MWCNT's (multi wall carbon nano tubes)

3, Mega tubes :- this type of fullerene having large dimensions.

4, Polymers :- the two dimensional and three dimensional polymers generates fullerenes in the presence of high temperature and pressure.

5, Nano onions : the fullerene which exhibits multiple layers like onions is known as nano onions.

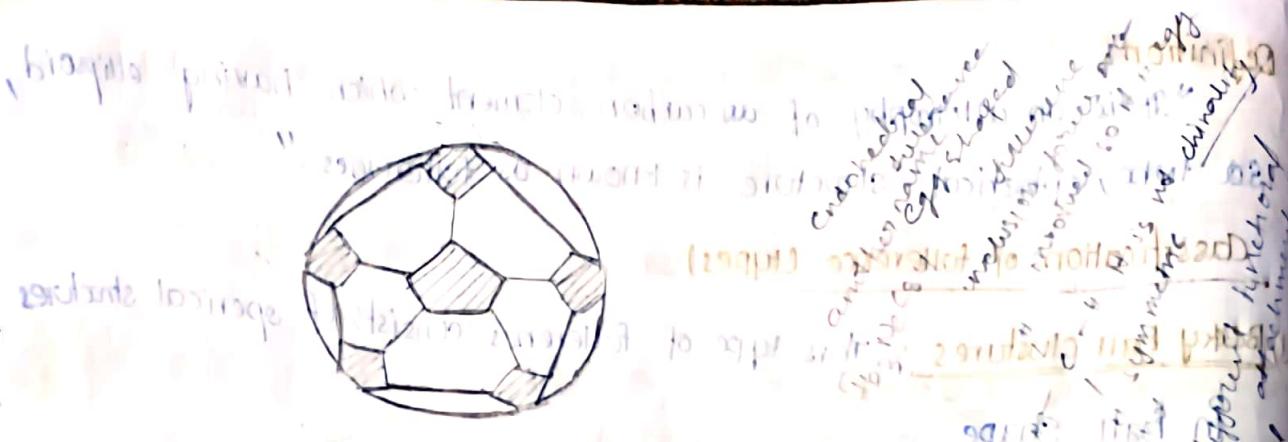
6, linked ball and chain dimers : the soccer ball shape of fullerenes connected in chainwise manner to form linked ball and chain dimers.

C_{60} fullerene (or Buckminsterfullerene) → The atropack name of C_{60} fullerene is truncated icosahedron

In this carbon element undergoes sp^2 hybridisation with bond length 1.4 \AA at bond angle 120° .

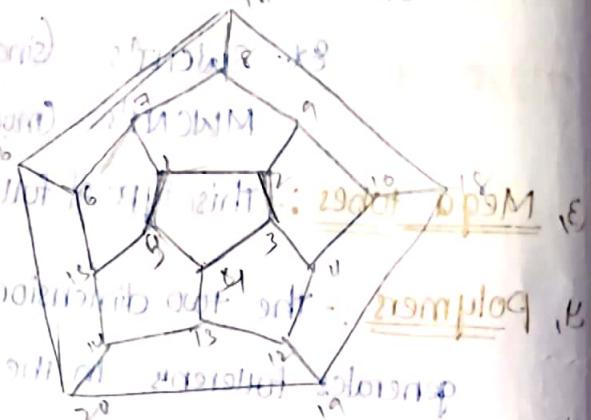
→ In C_{60} fullerenes we have 12 pentagonal rings and 20 hexagonal rings.

→ smaller ring (C_{20}) has 12 pentagonal rings and 12 hexagonal rings.



C₆₀ fullerene

The IUPAC name of C₆₀ fullerene is unsaturated dodecahedran. It is very smallest fullerene molecule.



Properties:

1, Endohedral fullerenes: whenever the atoms tapped into inside of the fullerenes which gives inclusion compound like egg shaped
Ex: Tb₃N₆C₈₄

3, chirality:

In fullerene carbon element exhibits chirality which means different functional groups attached to carbon element.

3, sculpture property: According to Quantum mechanics fullerene exhibits

both dual nature that's why these are used to sculpturing of ceramics

4, solubility :- fullerenes are sparingly soluble in organic solvents like carbon disulphide, and toluene.

5. Halogenation: the addition of halogens like fluorine, chlorine, bromine to the fullerenes which forms halogenated fullerenes
Ex: $C_{60}Br_8$, $C_{60}Br_{24}$ (Bromine is preferable)

6. Hydrogenation: the addition of hydrogens to the fullerenes which forms polyhydro fullerenes

7. Addition of Hydrogen: the addition of oxygen, ozone to the fullerenes which forms epoxide state of fullerenes
Ex: $C_{60}O$

(epoxide: if one C is exchanged by oxygen atom)
is called epoxide structures

Applications
→ It is used to prepare hydrogen fuel with the help of polyhydro fullerenes.

→ In medical field fulleren materials are used to control HIV (Human Immuno deficiency of virus)
→ fullerenes are used to prepare solar cells

Carbon Nano tube (CNT's)

Sumio Iijima proposed carbon nanotubes in 1991
arc discharge method

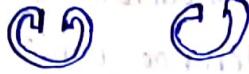
"It is an allotropy of carbon element which consists of continuous unbreakable hexagonal rings in cylindrical structure with 0.4 nm is known as carbon nanotubes"

Types of carbon nanotubes:

① SWCNT's: This type of carbon nanotube have monolayer of hexagonal ring sheets is known as SWCNT's

② MWCNT's (multiwall carbon nano tubes):
In this carbon nanotube two or more hexagonal ring sheets are attached.

MWCNT's
perchman model (edges)
Russian double model (no edges)

3) Torus : Doughnut shape  

4, Nanobud :- The fullerenes are attached either top side or bottom side to the carbon nano tubes. 

5, N-doped CNT's :- The addition of 15th group elements to the carbon Nano tubes is known as N-doped carbon nanotubes.

6, Peapod :- The internal attachment of fullerene to the Carbon nanotube is known as peapod

7, Graphenated CNT's

8, Cup - stacked :- Arranged in cupwise manner.

Properties

① tensile strength

(27 GPa) giant arch model

② Hardness —

bullet proof vest

③ Telescopic length ability to shorten up to 10%

④ Semiconductor disregard of band gap

⑤ toxicity

harmful to health after inhalation

⑥ Electro magnetic radiation absorption model to 2000

⑦ thermal conductivity electrons can't jump from layer to layer

Applications of CNT's bullet proof vest radioisotopes very light

1, These are used in preparation of space elevators, stab proof

Bullet proof clothing, bullets protection

2, solar cells protect sunlight

3, food storage containers. prevent oxidation oxygen

④ paper batteries mixing of cellulose derivatives.

⑤ antibacterial fabrics

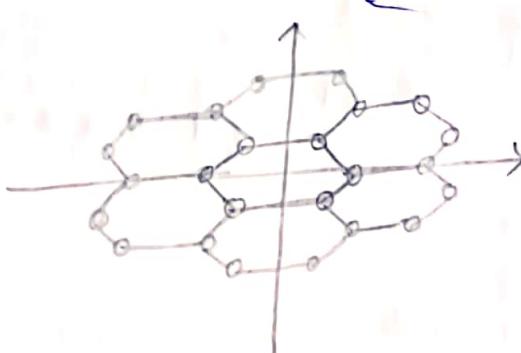
Graphene nanoparticles: A

atom lattice of graphite prepared by Andrei Geim & Konstantin Novoselov prepared Graphene

nano particles in 2003 during cleaning of graphite wasteage.

They awarded nobel prize in 2010.

"It is an allotropy of carbon element which having unbreakable monolayer of hexagonal ring with honeycomb lattice structure is known as graphene nano particles."



Graphene nanoparticles are zero band gap conductors because of valency band conduction band connected at one advance specific centre which is known as dirac point.

preparation of Graphene

i. Top down approach

mechanical exploitation

chemical exploitation

b) mechanical exploitation: During this process we apply mechanical energy after that we get nanoparticles.

→ our scientist prepared Graphene nanoparticles by using mechanical exploitation method.

b) chemical exploitation: During this process we use alkali metals as a chemical

ii. Bottom up approach

CVD

Atomic Layer deposition

a) chemical vapour deposition:

The carbon element compounds undergoes cooling phase. In the presence of nickel metal as substrate we get graphene nano particles.

b) atomic layer deposition:

Properties of Graphene:

1, strongest material

2, thinnest material.

3, young modulus

4, transmittance is 98%.

5, high conductivity

6, thermal stability ($5000 \text{ W m}^{-1} \text{ K}^{-1}$)

7, flexible

8, zero band gap

9, little scattering

10, semiconductor

11, transparency.

Applications

Integrated circuits, transistors, desalination, gas sensors,

Solar cells, flexible mobiles, water purifier, pollutant gases

Graphene paper