

## Postulates of Molecular Orbital Theory

Molecular Orbital Theory was given by [R.S. Mulliken and F. Hund](#).

According to MOT the [valence electrons are associated with all the nuclei in the molecule](#).

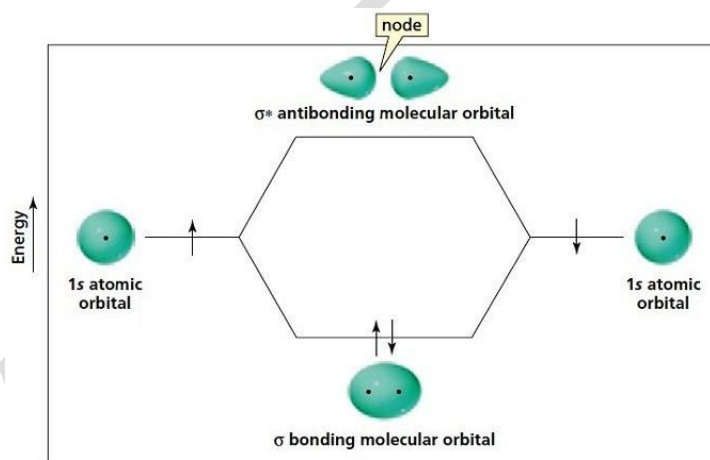
1. Atomic orbitals with same energy & symmetry combine to form molecular orbitals by LINEAR COMBINATION OF ATOMIC ORBITALS (LCAO)

If  $\Psi_A$  &  $\Psi_B$  are wave functions of atoms A & B then according to LCAO =

$$\Psi_{M.O} = \Psi_A \pm \Psi_B$$

Two types of molecular orbitals are formed: [bonding and antibonding molecular orbitals](#). Molecular orbitals formed the additive overlap of two atomic wave functions is known as [Bonding Molecular orbital](#) i.e.  $\Psi_b = \Psi_A + \Psi_B$

Molecular orbitals formed by subtractive overlap of two atomic orbitals wave function is called [Anti-bonding molecular orbital](#) i.e.  $\Psi_a = \Psi_A - \Psi_B$



2. The no. of molecular orbitals formed is always equal to the number of atomic orbitals taking part in bond formation.
4. Energy level of bonding M.O. is less than that of individual atomic orbitals. So,  $e^-$  present in bonding M.O stabilizes the molecule.  
Energy level of antibonding M.O is more than that of individual atomic orbitals. So  $e^-$  present in anti-bonding M.O destabilizes the molecule.
5. Molecular orbitals that do not participate in bonding are called non-bonding M.O & their energy is equal to that of individual atomic orbitals.
6. [Molecular orbitals are polycentric](#).
7. [The atomic orbitals involved in the formation of M.O. completely lose their identity after the formation of molecular orbitals](#).
8. Electrons filling in the molecular orbitals follow Aufbau principle, Pauli's exclusion principle & Hund's rule of maximum multiplicity.
9. The electrons are filled in the molecular orbitals according to the following order:  
[From  \$H\_2\$  to  \$N\_2\$ :  \$\sigma 1s, \sigma^\* 1s, \sigma 2s, \sigma^\* 2s, \pi 2px = \pi 2py, \sigma 2pz, \pi^\* 2px = \pi^\* 2py, \sigma^\* 2pz\$](#)   
[From  \$O\_2\$  to  \$Ne\_2\$ :  \$\sigma 1s, \sigma^\* 1s, \sigma 2s, \sigma^\* 2s, \sigma 2pz, \pi 2px = \pi 2py, \pi^\* 2px = \pi^\* 2py, \sigma^\* 2pz\$](#)

10. Molecules or ions with one or more unpaired  $e^-$  in molecular orbitals are **paramagnetic** while those with all paired electrons in M.O. are called **diamagnetic**.
11. Stability & strength of a chemical bond is expressed in terms of bond order.
12. **B.O.** – Bond order is equal to one half of the difference between the number of electrons in bonding M.O & the no. of  $e^-$  is antibonding M.O.

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

$N_b$  = electrons in B.M.O.;  $N_a$  = electrons in anti B.M.O.

$$B.O. \propto \frac{1}{B.L.} \propto \text{Stability} \propto \text{Bond Dissociation Energy}$$

### Significance of bond order:

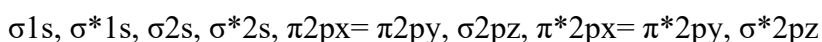
- Zero B.O.: Molecule is unstable does not exist.
- Negative bond order is not possible.
- Positive value of B.O.: Molecule exists & is stable.
- Bond order of +1, +2, +3 indicates the molecule has single, double or triple bond respectively.
- $B.O. \propto \text{Bond Energy} \propto \text{Bond angle} \propto \text{Stability} \propto \frac{1}{B.L.}$

### Differences between molecular orbitals and atomic orbitals.

BONDING MOLECULAR ORBITALS	ANTIBONDING MOLECULAR ORBITALS
1. They are formed by additive overlapping of atomic orbitals.	They are formed by subtractive overlapping of atomic orbitals.
2. $\Psi_b = \Psi_A + \Psi_B$ (A and B are two atomic orbitals)	$\Psi_a = \Psi_A - \Psi_B$ (A and B are two atomic orbitals)
3. Electrons contribute to the formation of bond.	Electrons do not contribute to the formation of bond.
4. They have low energy and high stability.	They have high energy and low stability.
5. They are shown as $\sigma, \pi$ etc.	They are shown as $\sigma^*, \pi^*$ etc.
6. Maximum electrons are located in between the two nuclei.	Electrons are scattered.
7. Electron density is higher.	Electron density is lower.

### HOMODIATOMIC MOLECULES: Molecules with same atoms.

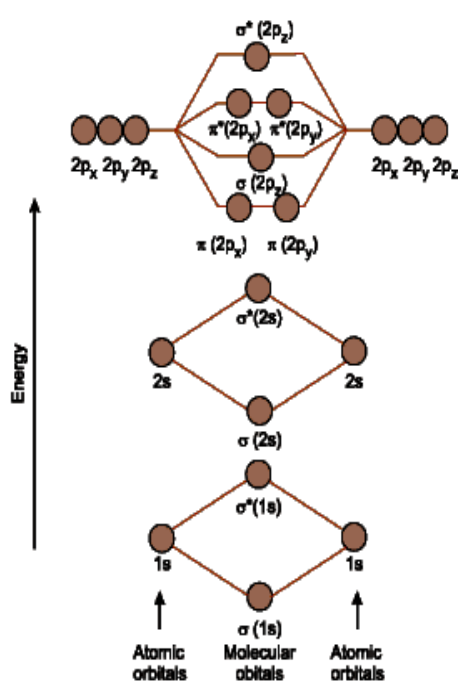
From  $H_2$  to  $N_2$  :



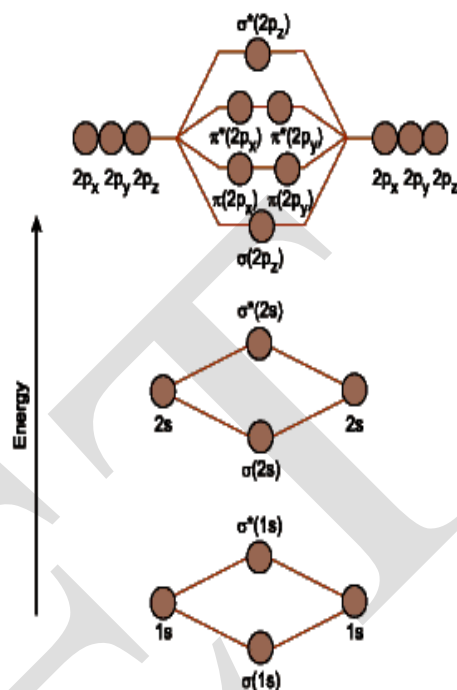
From  $O_2$  to  $Ne_2$  :



## MO diagram for molecules from Li<sub>2</sub> to N<sub>2</sub>



## MO diagram for molecules from O<sub>2</sub> to Ne<sub>2</sub>



## Molecular Orbital Diagrams of various homo-diatomic molecules

Hydrogen forms diatomic molecule while helium remains monoatomic.

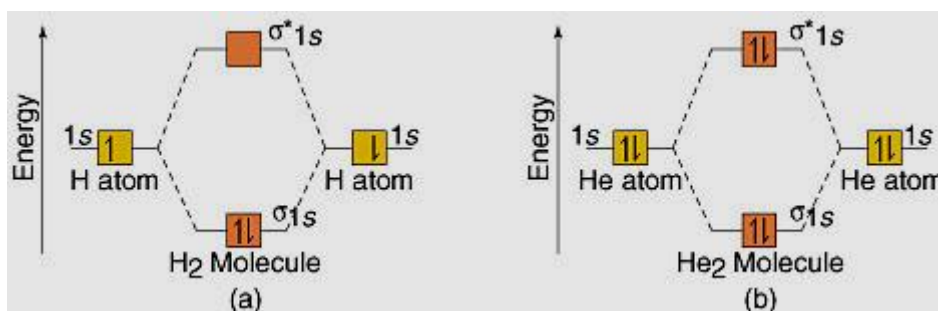
Or

Helium molecule does not exist in nature.

$$H_2 \rightarrow \sigma 1s^2 \text{ B.O} = \frac{1}{2}(N_b - N_a) = \frac{1}{2}(2 - 0) = 1$$

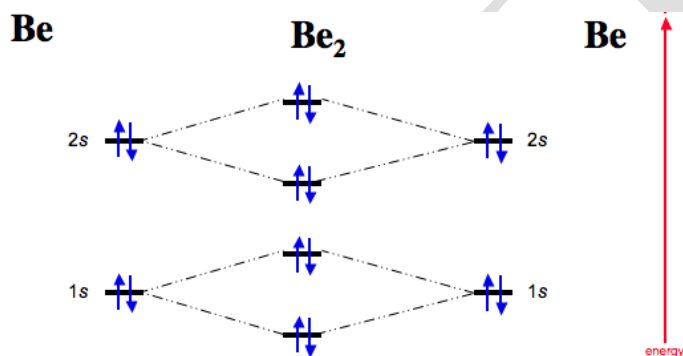
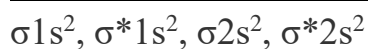
$$He_2 = \sigma 1s^2 \sigma^* 1s^2 \text{ B.O} = \frac{1}{2}(N_b - N_a) = \frac{1}{2}(2 - 2) = 0$$

As the bond order of He<sub>2</sub> is zero, the molecule (diatomic) cannot be formed and it remains monoatomic. B.O of H<sub>2</sub> is 1, so it is a stable molecule.



## Be<sub>2</sub> does not exist in nature:

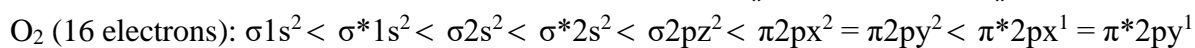
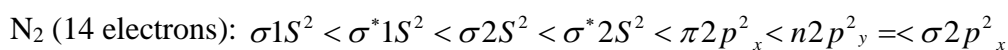
Molecular electronic configuration of Be<sub>2</sub> (8e<sup>-</sup>):



$$B.O = \frac{1}{2}(N_b - N_a) = \frac{1}{2}(4 - 4) = 0$$

Since bond order is zero the molecule cannot be formed.

## N<sub>2</sub> is diamagnetic & O<sub>2</sub> is paramagnetic



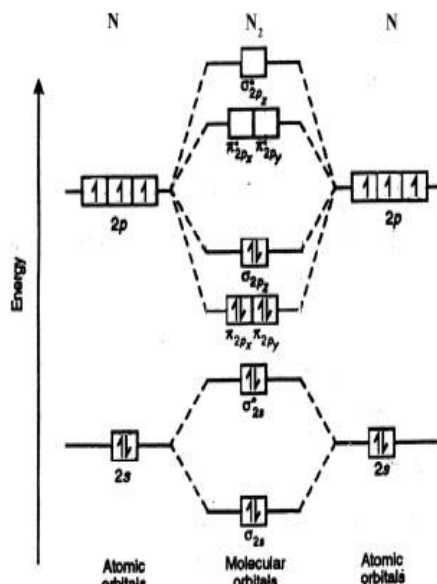
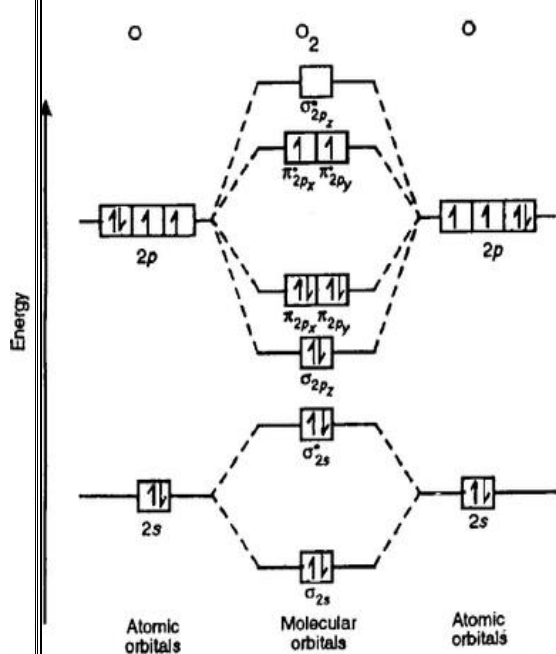


Fig. Molecular orbital energy level diagram of  $N_2$

Molecular Orbital Diagram of  $O_2$  Molecular Orbital Diagram of  $N_2$

**Oxygen is paramagnetic** as in molecular orbital diagram of oxygen there are two unpaired electrons in  $\pi^*2p_x$  and  $\pi^*2p_y$ .

**Nitrogen is diamagnetic** as all the electrons in its molecular orbital diagram are paired.

**Bond energy of  $N_2$  is greater than bond energy of  $O_2$**

$$\text{Bond Energy} = \text{Bond order}$$

$$\text{B.O. of } N_2 \text{ B.O.} = \frac{1}{2}(N_b - N_a) = \frac{1}{2}(10 - 4) = \frac{1}{2} \times 6 = 3$$

$$\text{B.O. of } O_2 \text{ B.O.} = \frac{1}{2}(N_b - N_a) = \frac{1}{2}(10 - 6) = \frac{1}{2} \times 4 = 2$$

Since bond order of  $N_2$  is greater than that of  $O_2$ , hence its Bond Energy is greater than that of  $O_2$ .

**$F_2$  is diamagnetic while  $O_2$  is paramagnetic.**

MO electronic configuration of  $F_2$  ( $18e^-$ )

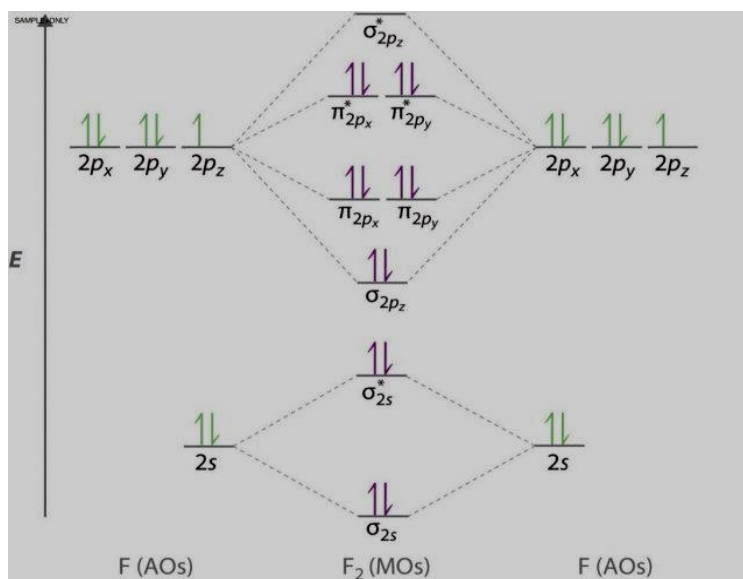
$$\sigma 1s^2 < \sigma^* 1s^2 < \sigma 2s^2 < \sigma^* 2s^2 < \sigma 2p_z^2 < \pi 2p_x^2 = \pi 2p_y^2 < \pi^* 2p_x^2 = \pi^* 2p_y^2$$

All the electrons in molecular orbitals are paired so, it is diamagnetic.

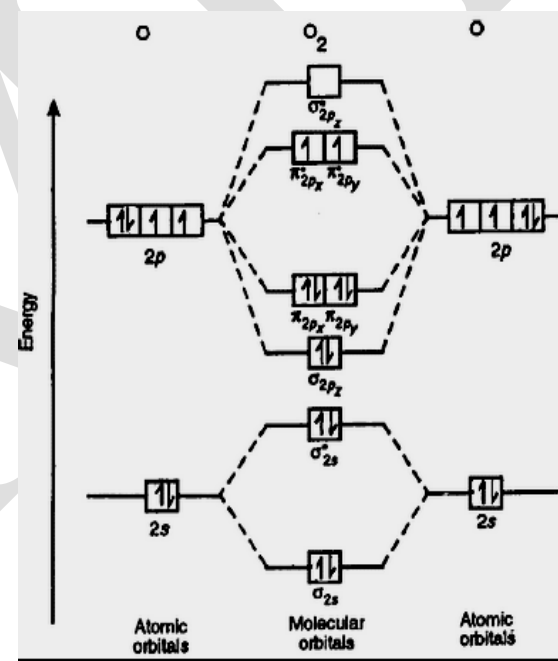
MO electronic configuration of  $O_2$  ( $16e^-$ )

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

There are two unpaired electrons in  $\pi^*2p_x$  &  $\pi^*2p_y$ ; So,  $O_2$  is paramagnetic



Molecular Orbital Diagram Of Fluorine Molecule

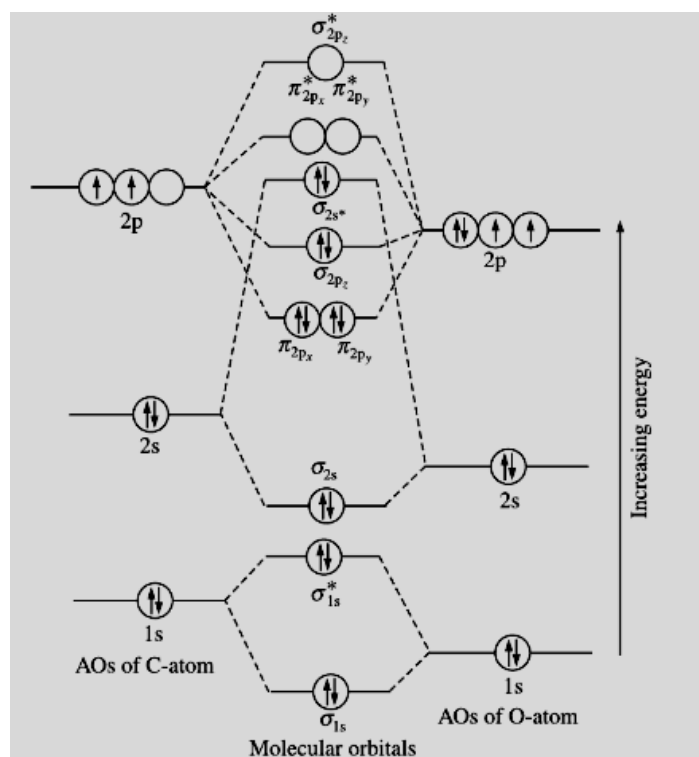


Molecular Orbital Diagram Of Oxygen Molecule

## Heteronuclear Diatomic Molecules

- Diatomic molecules with two different atoms are called heteronuclear diatomic molecules.
- A molecular orbital energy-level diagram is always skewed toward the more electronegative atom.

## Molecular orbital diagram of CO:



The MO configuration of CO is  $(\sigma_{1s}^b)^2 < (\sigma_{1s}^*)^2 < (\sigma_{2s}^b)^2 < (\pi_x^b)^2 = (\pi_y^b)^2 < (\sigma_{2p_z}^b)^2 < (\sigma_{2s}^*)^2 < (\pi_x^*)^0 = (\pi_y^*)^0$

$$\begin{aligned} \text{Bond order} &= \frac{1}{2} [N_b - N_a] \\ &= \frac{1}{2} [10 - 4] = 3 \text{ (stable bonds)} \end{aligned}$$

In case of  $\text{CO}^+$ , one electron from  $\sigma_{2s}^*$  anti-bonding molecular orbital is lost.

The MO configuration of  $\text{CO}^+$  is  $(\sigma_{1s}^b)^2 < (\sigma_{1s}^*)^2 < (\sigma_{2s}^b)^2 < (\pi_x^b)^2 = (\pi_y^b)^2 < (\sigma_{2p_z}^b)^2 < (\sigma_{2s}^*)^1$

$$\begin{aligned} \text{Bond order} &= \frac{1}{2} [N_b - N_a] \\ &= \frac{1}{2} [10 - 3] = 3.5 \text{ (stable bonds)} \end{aligned}$$

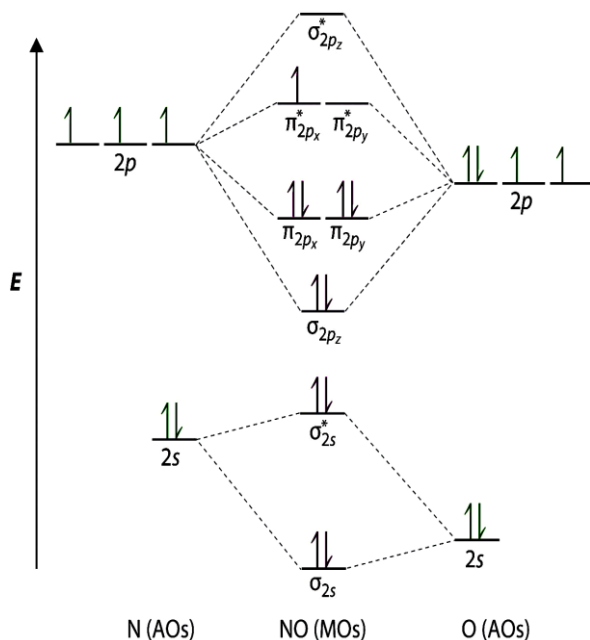
Since the bond order of  $\text{CO}^+$  is greater than CO, so  $\text{CO}^+$  is more stable.

CO is diamagnetic in nature whereas  $\text{CO}^+$  is paramagnetic.

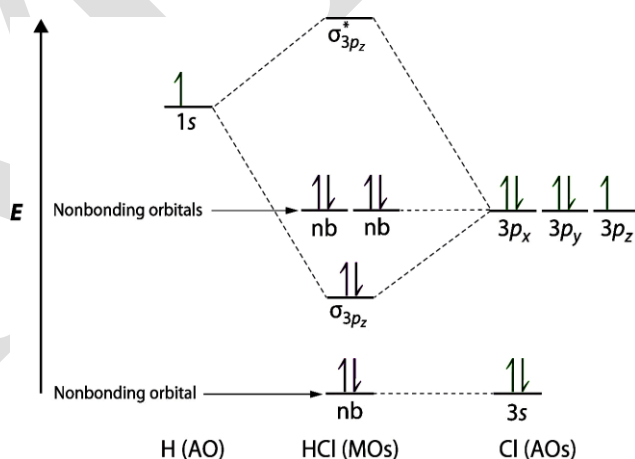
## Molecular orbital diagram of NO, its bond order and its magnetic behaviour.

$$B.O. \text{ of } NO = \frac{1}{2}(N_b - N_a) = \frac{1}{2}(7 - 3) = 2$$

NO is paramagnetic in behaviour as it contains an unpaired electron in  $\pi^*2p_x$  orbital.



## Molecular orbital diagram of HCl, bond order and magnetic behaviour.

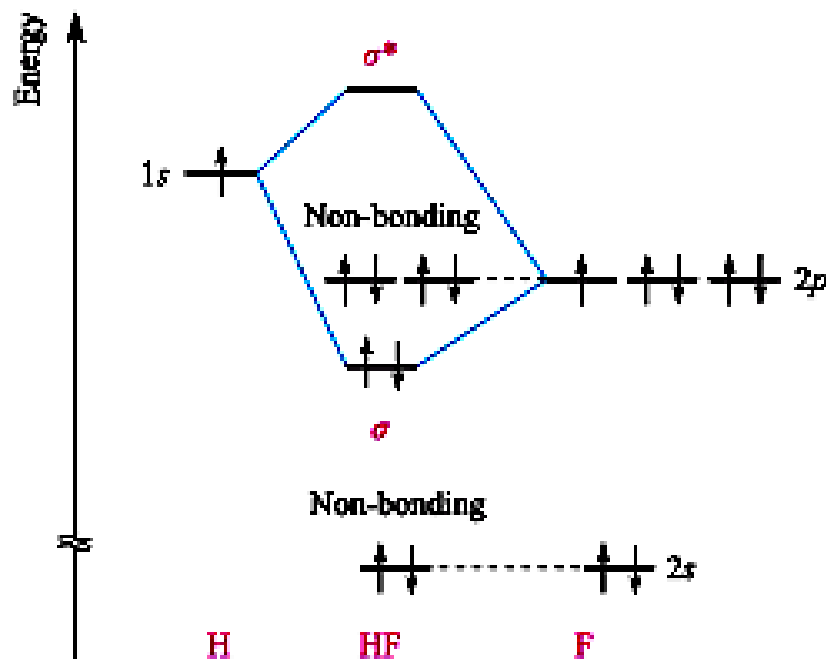


HCl is diamagnetic in nature as all the electrons in its molecular orbital diagram are paired.

$$B.O. \text{ of } HCl = \frac{1}{2}(N_b - N_a) = \frac{1}{2}(2 - 0) = 1$$



## Molecular Orbital Diagram of HF:

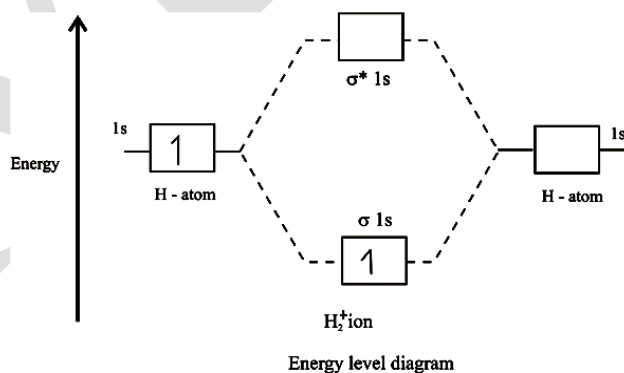


$$B.O. = \frac{1}{2}(N_b - N_a) = \frac{1}{2}(2 - 0) = \frac{1}{2} \times 2 = 1$$

HF is diamagnetic in nature.

## Molecular orbital Diagrams of Molecular ions:

### Molecular orbital diagram of $H_2^+$ ( $1e^-$ ) ( $\sigma 1s^1$ ).

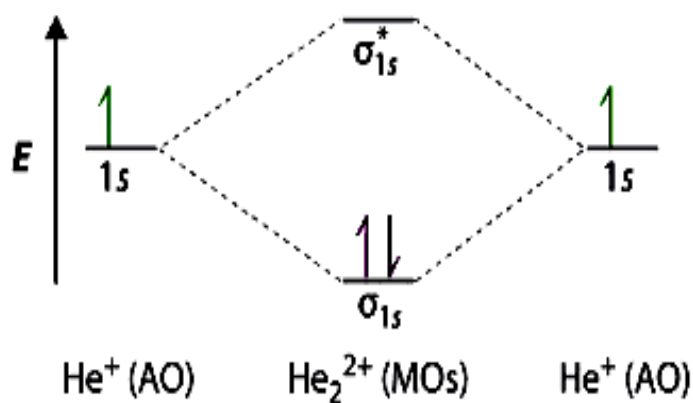


$$B.O. = \frac{1}{2}(N_b - N_a) = \frac{1}{2}(1 - 0) = .5$$

Less stable than  $H_2$  as its bond order is less than  $H_2$ .

It is paramagnetic in nature.

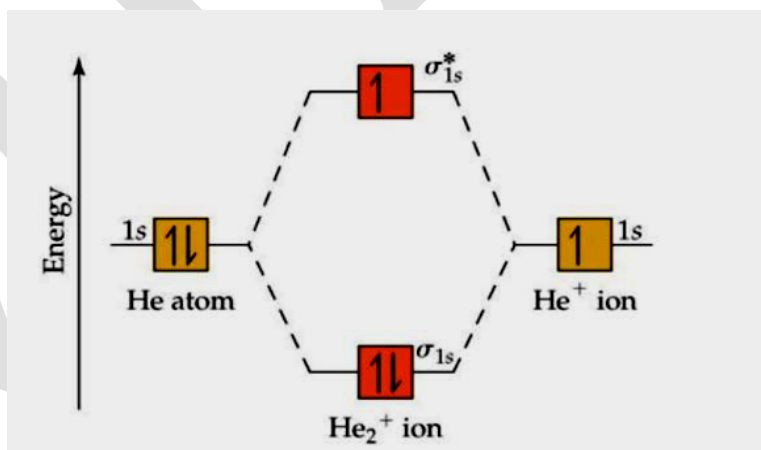
**M.O. Diagram of  $\text{He}_2^{2+}$ :** Isoelectric with  $\text{H}_2$



Molecular configuration:  $\sigma 1s^2$  ;

Bond Order =  $\frac{1}{2}(\text{N}_b - \text{N}_a) = \frac{1}{2}(2 - 0) = 1$ ; It is diamagnetic in nature.

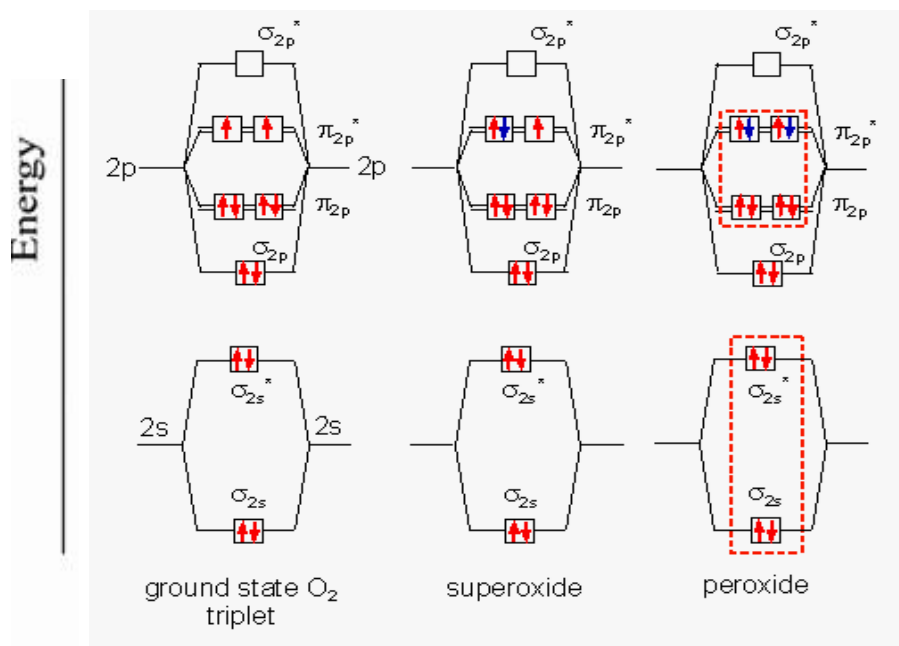
**$\text{He}_2^+$** :  $\sigma 1s^2 \sigma^* 1s^1$



B.O of  $\text{He}_2^+ = \frac{1}{2}(\text{N}_b - \text{N}_a) = \frac{1}{2}(2 - 1) = 0.5$

It is paramagnetic in behaviour due to presence of unpaired electron.

## Molecular orbital diagrams of superoxide ( $O_2^-$ ) and peroxide ( $O_2^{2-}$ ) molecular ions.



$$\text{B.O. of } O_2^- = \frac{1}{2}(N_b - N_a) = \frac{1}{2}(8 - 5) = 1.5; \quad \text{B.O. of } O_2^{2-} = \frac{1}{2}(N_b - N_a) = \frac{1}{2}(8 - 6) = 1$$

Since, B.O.  $\propto$  stability. So, the order of stability will be  $= O_2 > O_2^- > O_2^{2-}$

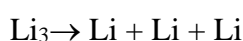
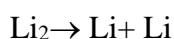
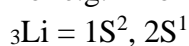
**Metallic Bond:** "The force of attraction that holds the metal ions and the free electrons within its sphere of influence is known as metallic bond".

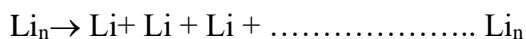
## BAND THEORY

### Explanation of Metallic bond on the basis of M.O.T. or band theory of Solids

- \*According to this theory electron in the metal are considered to cover the whole crystal lattice and are not localized between any two atoms.
- \*So, metallic bond is formed by the delocalization of all the orbitals containing free electrons.
- \*According to M.O.T. when two atomic orbitals combine two molecule orbitals are formed i.e. bonding and anti-bonding.
- \*When three atomic orbitals combine, three M.O.'s are formed i.e. bonding, non-bonding & anti-bonding mol. orbitals.
- \*Similarly when 'n' atomic orbitals combine, 'n' molecular orbitals are formed.
- \*In case of metals 'n' is of the order of  $10^{23}$ . So,  $10^{23}$  molecules orbitals are formed and these are so closely spaced that they form a continuum (continuous energy band). That is why the theory is known as band theory.

For e.g. - Bonding in Lithium Metal





## Band Theory for Lithium

MOs produced by linear combination of the 2s orbitals in  $\text{Li}_2$ ,  $\text{Li}_3$  and  $\text{Li}_4$ .

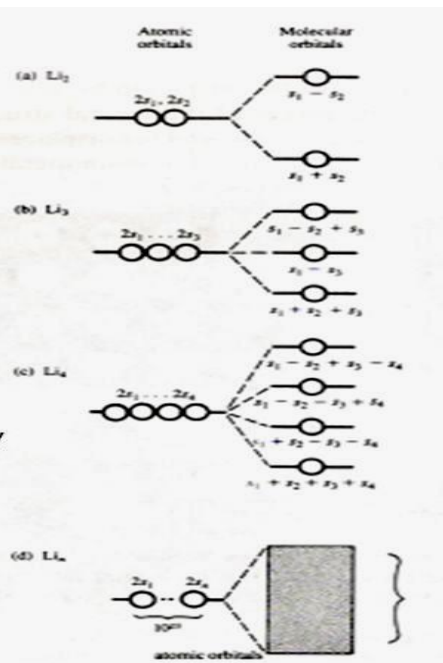
Note that, for every atom added:  
An additional MO is formed

The energies of the MOs get closer together

When a sample contains a very large number of Li atoms  
(e.g.  $6.022 \times 10^{23}$  atoms in 6.941 g),

The **states** formed are so close in energy that they form a **band** of energy levels.

A band is named for the AOs from which it was made (e.g. **2s band**)



### Application of band theory:

It differentiates solids into conductors, semiconductors and insulators. This classification depends upon the width of energy gap or band gap or forbidden gap (energy bands do not exist in this region).

### Classification of solids into conductors, semiconductors and insulators on the basis of molecular orbital theory or band theory.

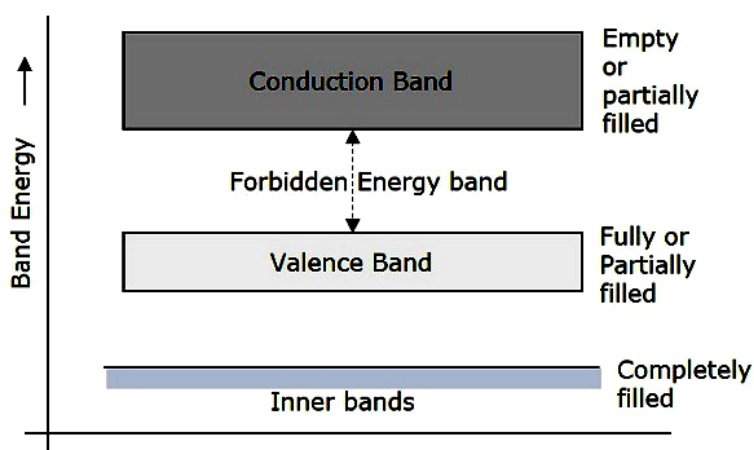
With the help of band theory we can classify solids into conductors, semiconductors and insulators. In case of solids there are three bands:

The outermost completely filled or partially filled (e.g. Lithium) energy band is known as valence band.

The band above the valence band that is empty at 0 K is known as conduction band.

The energy gap between valence & conduction band is known as Energy Gap or band gap or forbidden gap.

These bands are important from the conductivity point of view.



Formation of various bands in solids

The classification of materials into insulators, conductors and semiconductors mainly depends on the widths of the forbidden energy gap.

## Conductors:

In conductors there is no forbidden gap between valence band and conduction band. The two bands overlap. Hence even at room temperature, a large number of electrons are available for conduction. E.g. iron

## Insulators:

In case of such insulating material, there exists a large forbidden gap in between the conduction band and the valence band i.e. of the order of about 7 eV.

It is impossible for an electron to jump from the valence band to the conduction band. Hence such materials cannot conduct electricity and are called insulators.

Example: diamond, glass, wood, mica, paper etc.

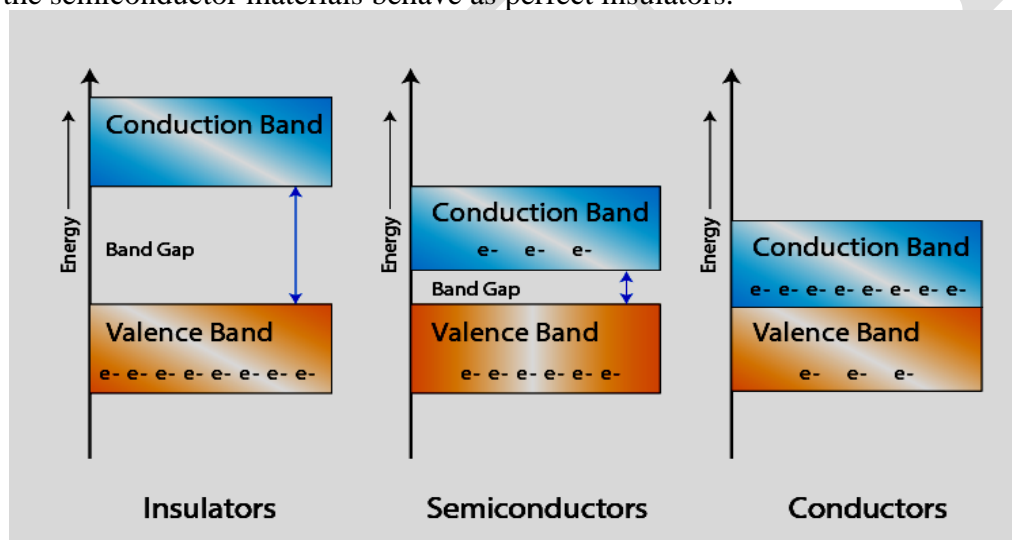
## Semiconductors:

Semiconductors are neither insulators nor conductors. The forbidden gap in such materials is in between conductors and insulators i.e. of the order of 1 eV. Such materials are called semiconductors.

For such materials, the energy provided by the heat at room temperature can lift the electrons from the valence band to the conduction band.

Therefore at room temperature, semiconductors are capable of conduction. But at 0 K or absolute zero (-273 °C), all the electrons of semiconductor materials find themselves locked in the valence band.

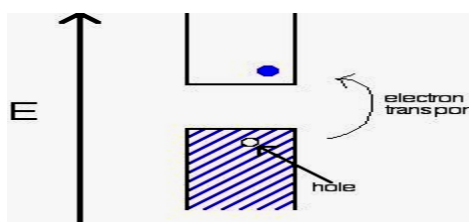
Hence at 0 K, the semiconductor materials behave as perfect insulators.



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

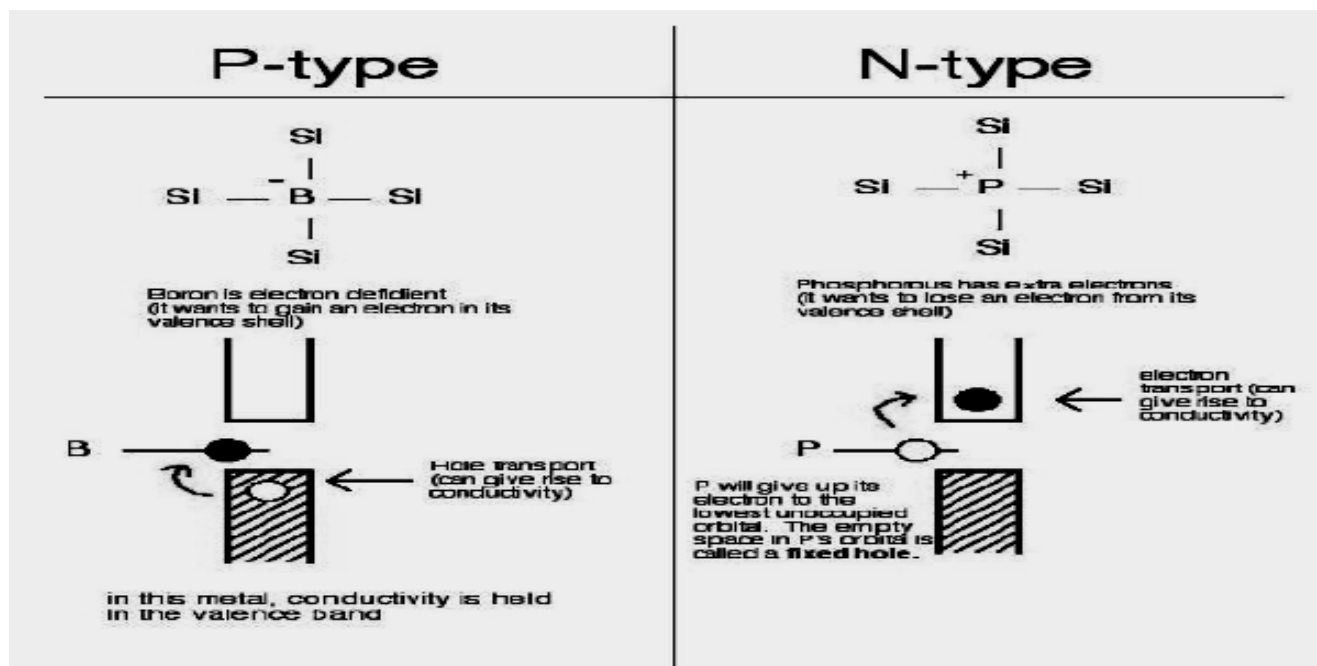
### **i. Intrinsic Semiconductors:**

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**. There are two different kinds of

extrinsic semiconductors, p-type (positive charge doped) and n-type (negative charge doped) depending on the type of impurity.



S.No	Conductors	Semiconductors	Insulators
1	Easily conducts the electrical current.	Conducts the electric current less than conductor and greater than insulator.	Does not conduct any current.
2	Has only one valence electron in its outermost orbit.	Has four valence electron in its outermost orbit.	Has eight valence electron in its outermost orbit.
3	Conductor formed using metallic bonding.	Semiconductors are formed due to covalent bonding.	Insulators are formed due to ionic bonding.
4	Valence and conduction bands are overlapped.	Valence and conduction bands are separated by forbidden energy gap of 1.1eV.	Valence and conduction bands are separated by forbidden energy gap of 6 to 10eV.
5	Resistance is very small	Resistance is high	Resistance is very high
6	It has positive temperature coefficient	It has negative temperature coefficient	It has negative temperature coefficient
7	Ex: copper,aluminium,etc	Ex: silicon, germanium, etc	Ex: Mica, Paper, etc



## Properties of metals:

1. **Lustrous:** All the metals have shining appearance which is known as metallic lustre.

**Reason:** When light falls on the surface of metals, the loosely held electrons (free  $e^-$ ) absorb photons of light and get excited to higher energy levels. They drop back from their higher energy level to original energy level and thus emit the absorbed light, which appears as shine on metals surface.

2. **Good thermal and electrical conductors:**

**Thermal conductivity:** If we start heating a part of metal sheet, after some time the entire metal sheet gets heated.

**Reason:** When a part of metal is heated, the kinetic energy of electrons in that region increases, which then move rapidly to the cooler part and transfer their K.E. to the other electrons by the means of collisions. In this way heat travels from hotter to cooler parts of the metal making them good conductor of heat.

**Electrical conductivity:** If we connect metal to the source of electricity, they start conducting electricity.

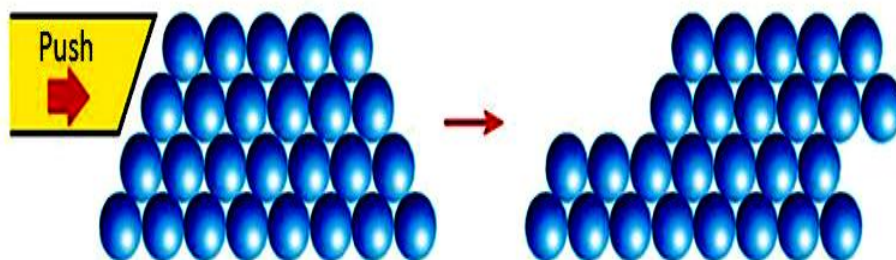
**Reason:** Metals conduct electricity due to presence of free mobile electrons. In the absence of electric field the free electrons in the metal lattice show random movement and so do not conduct electricity but in the presence of electric field, the electrons start moving readily towards anode (+ve electrode). Thus, they conduct electricity throughout the metal from one end to the other.

3. **Conductivity of metals decreases with rise in temperature:** Kinetic energy and thus vibrations of kernels increases with increase in temperature. These vibrating kernels interfere with the directed flow of electrons through the metal crystal which results in the decrease in conductivity of metals.

\*Conductivity of semiconductors increases with increasing temperature.

4. **Metals are malleable and ductile**

Metals are malleable (can be beaten into sheets) and ductile (can be drawn into wires) due is non-directional nature of metallic bond. The layers of atoms can slide over each other easily when force is applied. Hence, only the shape of metal (crystal) changes, the crystal structure does not change.



## Graphite: An allotrope of Carbon

### Structure of graphite:

Graphite is an allotrope of carbon (it is made up of only pure carbon atoms).

Each carbon atom in graphite is  $sp^2$  hybridised.

6 such carbon atoms join with the covalent bonds to form hexagons.

In hexagons each carbon atom forms three covalent bonds (C-C distance is  $1.42 \text{ \AA}$ ) with other carbon atoms.

Fourth electron of each carbon atom is free to move within the layer.

Various hexagons join together to form a plane or sheet called graphene.

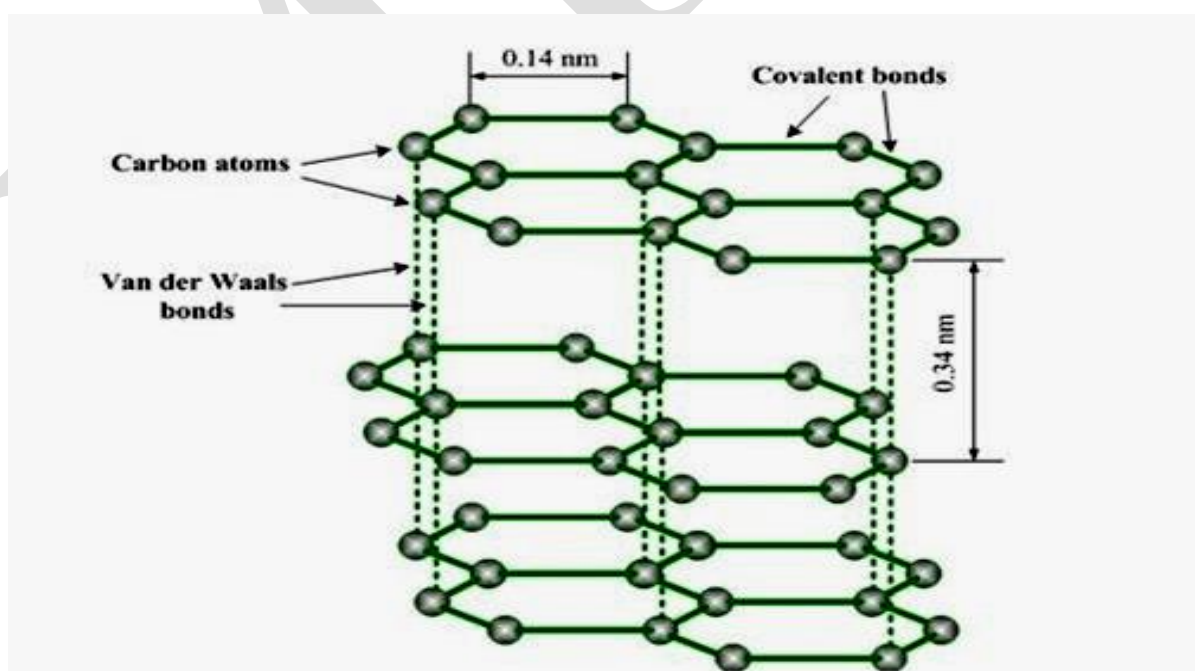
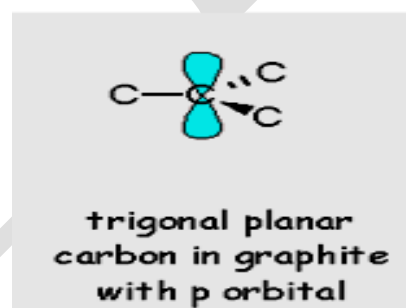
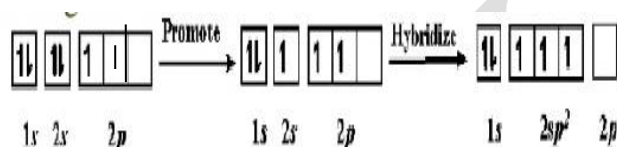
Various sheets (graphene) are arranged one above the other.

Different layers of graphite are attached to each other with weak Vander Waals forces.

Distance between two successive sheets is  $3.41 \text{ \AA}$ .

Graphite has planar, two dimensional structure.

Hybridisation of C in graphite:



### Structure Of Graphite



## Properties of Graphite:

1. It is greyish black and greasy substance.
2. Has metallic lustre and is opaque to light.
3. High Melting point because the strong covalent bonds take long time to break.
4. Slippery nature / Layers can slide one another due to weak Vander Waal forces of attraction between the two layers.
5. Low coefficient of friction.
6. Ineffective in vacuum conditions.
7. Thermodynamically more stable than diamond.
8. Graphite exists in two forms:  $\alpha$ -graphite (layers are arranged in sequence ABABAB..... with third layer exactly above the first layer) and  $\beta$ -graphite (layers in the sequence ABCABCABC.....).
9. In spite of being non-metal, **graphite is a conductor** due to the presence of free electron in  $p_z$  orbital of each carbon
10. Density  $1.25\text{g/cm}^3$

## Applications of Graphite:

- *Used as a lubricant* as layers can slide over one another due to weak vanderwaals forces.
- *Used in pencil leads* due to soft, slippery nature and it leaves a black mark on paper when rubbed against it.
- *Used in the preparation of electrodes* as it conducts electricity due to presence of free electron on each carbon atom.
- *Used to prepare crucible* due to high melting point.
- *Used as moderator in nuclear reactors* as it absorbs fast moving neutrons.
- *Used as a conductor of electricity* in batteries, solar panels etc.
- *Used in electrotyping and in making gramophone records.*
- It is a *component of printer's ink.*
- It is *lightest of all reinforcing materials.*

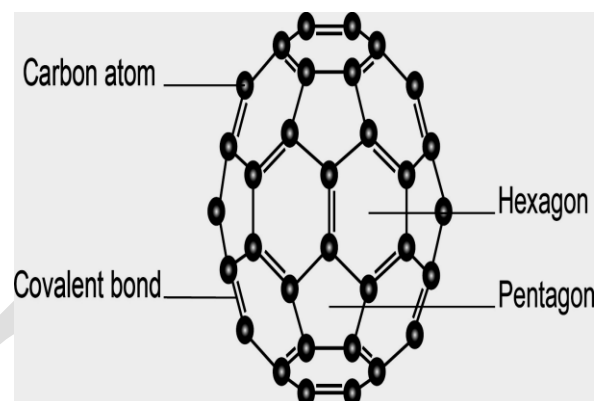
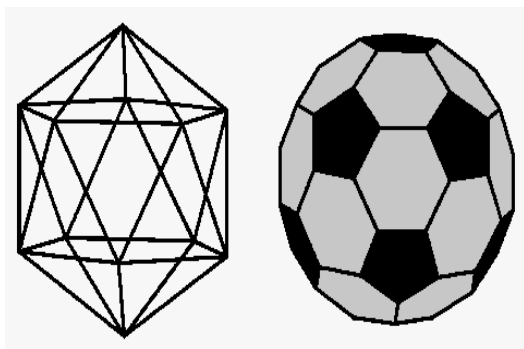
## Fullerene (Discovered by Kroto & Smalley)

- It is an allotrope of carbon, also called Buckminster fullerene or Bucky Ball.
- $\text{C}_{60}$  is the most stable & widely used member of fullerene family

### Structure:

- Made up of 60 carbon atoms.
- Each carbon atom is  $\text{sp}^2$  hybridised, forming three bonds and having one unpaired electron.
- There are 12 pentagons & 20 hexagons of C atoms.
- No two pentagons touch each other i.e. each pentagon is surrounded by hexagons from all the sides.
- Diameter of  $\text{C}_{60}$   $7\text{\AA}$ ; **geometry**-truncated icosahedron or geodesic dome.
- There are 30 ( $\text{C}=\text{C}$ ) double bonds in  $\text{C}_{60}$
- There are 60 vertices, 32 faces.

- C-C single bond length- $1.45\text{\AA}$ ; C=C double bond length= $1.38\text{\AA}$
- It is highly symmetrical molecular & is said as zero dimensional
- Has tendency to avoid double bonds in pentagon rings.
- Fullerene crystal structure is FCC.
- Its density is  $1.65\text{ gm/cc}$



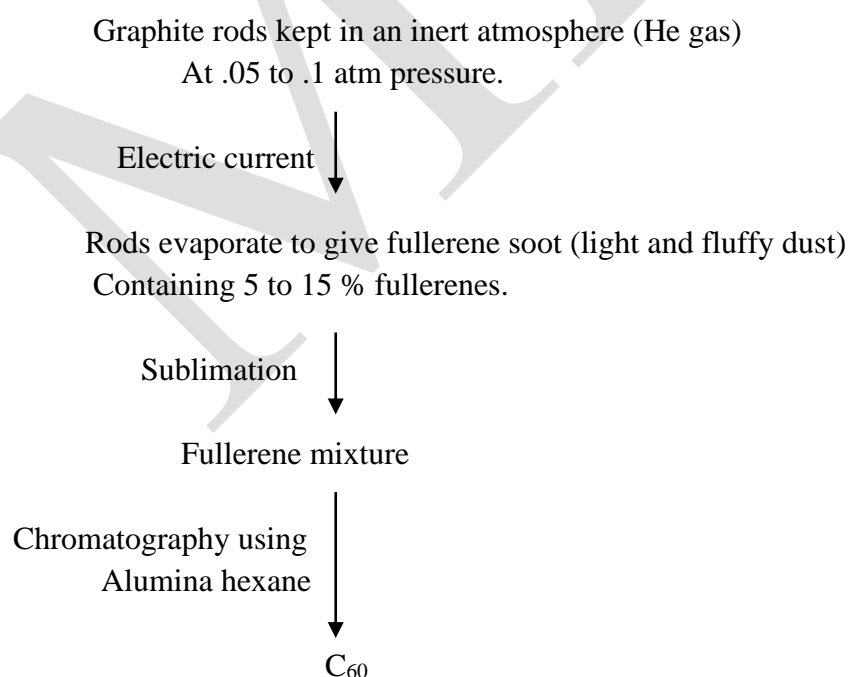
### **Preparation of Fullerene:**

Fullerenes are prepared by [Arc Discharge Method](#):

In this the graphite rods are vapourised in an inert atmosphere of helium gas.

Graphite rods evaporate to form a mixture of fullerenes ( $C_{60}$ ,  $C_{70}$  etc).

From this mixture pure  $C_{60}$  is isolated by column chromatography.



## Properties

- Mustard colored solid and looks brown and black as its thickness increases.
- Basically semiconductors but on doping with alkali metals can be converted into conductor or super conductor.
- Shows poor aromatic nature.
- Strongest known material to man.
- Exists as discrete molecule unlike graphite or diamond.
- Pentagon of a fullerene are more strained than the hexagon, so at higher temp., fullerene molecule break at pentagon sites.
- It is possible to trap some ions inside fullerene cage or attach some functional molecules to fullerene from outside.
- Can be compressed to lose 30% of its original volume, without destroying the carbon edge structure.

## Uses

- Have powerful antioxidant properties, so used in health & personal care areas.
- C<sub>60</sub> shows catalytic process.
- Act as drug delivery agent.
- C<sub>60</sub> derivatives act as potential inhibitors to HIV.
- Used in preparation of superconductors.
- In Optical devices.
- In preparation of soft Ferro magnets.
- Used in batteries as charge carriers.

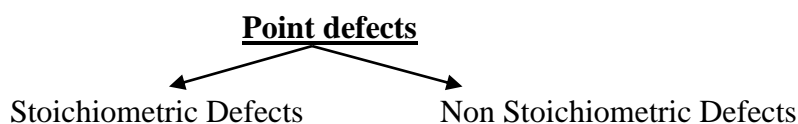
## CRYSTAL DEFECT OR CRYSTAL IMPERFECTION

Any deviation from a perfectly ordered arrangement of constituents (ions or atoms) in a crystal is known as crystal imperfection or defect.

Crystal defect may occur in three ways: at a point, along a line and over a surface.

**Point Defects or Zero dimensional defects:** When the deviation exists from the regular or periodic arrangement around an atom or a group of atom in a crystalline substance, the defects are called point defects. In these defects the deviation from orderly arrangement may occur in three ways:

- a) Absence of particles from their original site (Vacancy defect).
- b) Particles may be dislocated from original site (Interstitial defect).
- c) Presence of external impurities (Impurity defect).



## a) Stoichiometric Defects:

The compounds in which the number of +ve & -ve ions are exactly in the ratios indicated by their chemical formulas are called stoichiometric defects.

These defects do not disturb the stoichiometry (ratio of +ve & -ve ions) of solids.

Also known as thermodynamic defects as these occur due to increase in temperature.

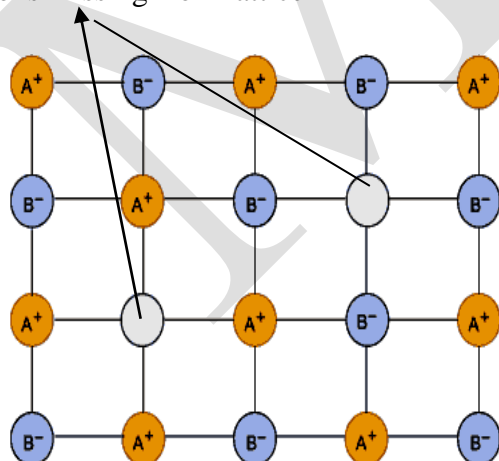
Increased temperature causes thermal vibrations of points.

These are of following types :

- Vacancy defects: Occurs when one or more atoms are completely missing from the lattice site creating a vacancy or hole. It decreases the density of the crystal. E.g. Schottky defect.
- Interstitial defects: Occurs when an atom occupies a position other than its normal lattice position. The density of the crystal remains the same. E.g. Frenkel defect.

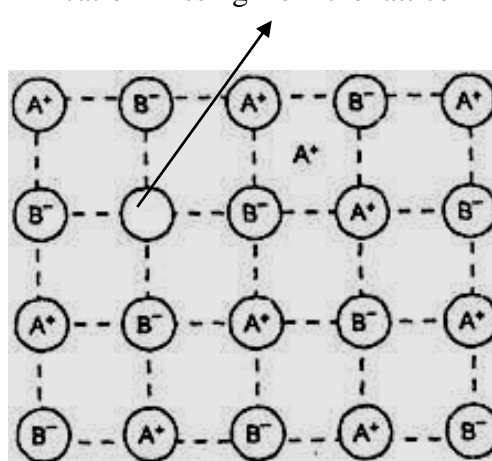
	<b>Schottky Defect</b>	<b>Frenkel Defect</b>
1	Equal no. of cations and anions are missing from crystal lattice.	An ion is missing from the lattice site and occupies interstitial position.
2	It is a vacancy defect.	It is a hybrid of vacancy defect & interstitial defect.
3	Occurs in highly ionic compounds, which have high coordination number.	Occurs in compounds with low coordination number.
4	Occurs in crystals having same size of anions & cations.	Occurs in crystal where cations & anions are of difference sizes (cations are smaller)
5	It decreases the density of the crystal.	Density of the crystal remains the same as before.
6	Found in pure alkali metal halides.	Not found in pure alkali metal halides as in them cations are large in size.
7	E.g. - NaCl, AgBr	e.g. - ZnS, AgCl, AgI, AgBr

Pair of ions missing from lattice



**Schottky Defect**

A cation missing from the lattice



**Frenkel Defect**

## Consequences of Schottky and Frenkel defects:

1. Presence of large number of schottky defects lowers the density of the crystal.
2. Closeness of charge brought about by Frenkel defects increases the dielectric constant of the crystal.
3. Compounds having such defects conduct electricity to small extent.
4. Due to presence of holes the lattice energy or the stability of the crystal decreases.
5. Too many holes may cause partial collapse of crystal.

## b) Non-Stoichiometric Defects :

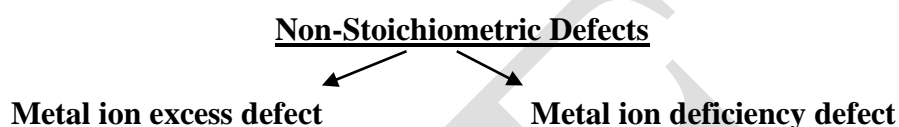
The defects which disturb the stoichiometry of the compounds are called Non-stoichiometric defects.

These are either due to the presence of excess metal ions or deficiency of metal ions.

Compounds with Non-stoichiometric defects are also known as Bertholide compounds.

Electrical neutrality of ionic crystal is maintained due to the presence of either extra positive charge on one of the neighbouring cation or presence of extra free electron in crystal lattice.

Cations are present in different oxidation states.



**Metal ion excess defect:** May be due to anionic vacancy or due to extra interstitial cation.

<b>Due to Anionic vacancy</b>	<b>Due to extra interstitial cation</b>
Arises when some of the negative ions (anions) are missing from the lattice site	Arises when the voids or interstitial sites are occupied by additional metal ions.
Absence of anion from the crystal lattice leaves a hole which is occupied by an electron to maintain electrical neutrality.	Electrical neutrality is maintained by corresponding number of electrons present in same interstitial site.
Crystals which are likely to show schottky defects show anionic vacancy defects.	Crystals which are likely to show Frenkel defects show such defects.
F centres or colour centres are created.	There are no F centres.
E.g. NaCl	E.g. ZnO

**Metal ion deficiency defect:**

<b>Due to cationic vacancy</b>	<b>Due to extra interstitial anion</b>
Arises when a cation is missing from its lattice.	Arises due to presence of extra anion at the interstitial site.
Occurs in ionic solids where metal ion can exhibit variable valency.	Not practically possible (Anions being large in size cannot occupy interstitial site).
To maintain electrical neutrality one of the nearest metal ion acquires the positive charge.	The extra negative charge is balanced by one extra positive charge on adjacent metal ion.
E.g. Transition metal compounds like NiO, FeO, FeS etc.	No examples known so far.

### **Consequences of metal excess and metal deficiency defects:**

Metal excess defects results in formation of n-type semiconductors whereas metal deficiency defect results in p-type semiconductors.

In metal excess defects flow of current is mainly due to presence of free electrons whereas in metal deficiency defect the current flows due to movement of positive holes.

### **IMPURITY DEFECTS:**

Impurity defects arises when foreign atoms i.e. atoms different from host atoms, are present in the crystal lattice. Germanium is common impurity in silicon. There are two types of impurity defects- Substitutional defects: when the host atom is substituted by some other atom.

Interstitial defects: When the atoms different from host atoms are present in the interstitial spaces.

## **Liquid Crystals**

Liquid Crystals are state of matter which has properties between those of conventional liquids and those of solid crystals. For example, a liquid crystal may flow like a liquid, but its molecules may be oriented in a crystal-like way.

The liquid-crystalline state is often called mesomorphic state (mezos meaning "intermediate"), and the liquid crystals are called mesophase.

Following character describe the crystalline structure.

- **Positional order**: the extent to which an average molecule or group of molecules shows translational symmetry (as crystalline material shows).
- **Orientalional order**: represents a measure of the tendency of the molecules to align along the director on a long-range basis.
- **Bond Orientalional Order**: describes a line joining the centres of nearest neighbour molecules without requiring a regular spacing along that line.
- Positional order + Orientalional order= crystal phase
- Varying Positional order + Orientalional order=LC phase

### **Essential requirements for a molecule to be a liquid crystal:**

- Shape of the molecule must be rod like or disc like.
- Molecule must be anisotropic in nature.
- Molecule must have some rigidity in its central region and the ends must be flexible.

### **Properties of liquid crystals:**

- The molecules are rod shaped or disc shaped.
- Molecules are anisotropic in nature.
- Assuming that the direction of preferred orientation in a liquid crystal (LC) is  $\uparrow$ , this direction can be represented by an arrow, called the director of the LC.
- Each molecule is orientated at some angle to the director.
- These molecules possess very strong dipole moment

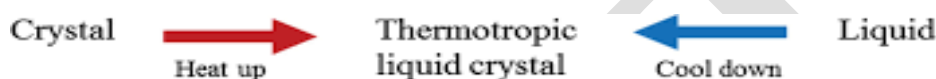
- The liquid crystal molecules prefer to align parallel to each other because of the strong intermolecular attraction ( $\pi$ - $\pi$  interaction)

### **Classification of liquid crystals:**

Liquid crystals are basically classified into:

1. Thermotropic liquid crystals
2. Lyotropic liquid crystals
3. Discotic Liquid Crystals

**1. Thermotropic liquid crystals:** They are formed by change of temperature. They occur as liquid crystals over a certain temperature range between the solid and liquid phase. Example – LCD TV's, alarm clocks.



These liquid crystals are further classified into:

- a) Nematic Liquid Crystals
- b) Smectic Liquid Crystals
- c) Cholesteric Liquid Crystals
- d) Discotic Liquid Crystals

**a) Nematic liquid crystals:** Word nematic is derived from the Greek word, 'Nema' which means "thread".

They show following properties:

- No positional order, but possess orientational order.
- It is only crystal phase with no long transitional order.
- Molecule have elongated rod like shape and are thread like.
- Do not have layered structure.
- Flow like normal liquids.
- They have low viscosity.
- Formed at relatively higher temperature.
- Can be aligned by the application of electric on magnetic field.
- Molecules are free to move in all the directions.
- Flow in all directions & not in layers.
- E.g.- p-azoxy anisole (first synthetic liquid crystal to be produced).

### **b)Smectic Liquid Crystals:**

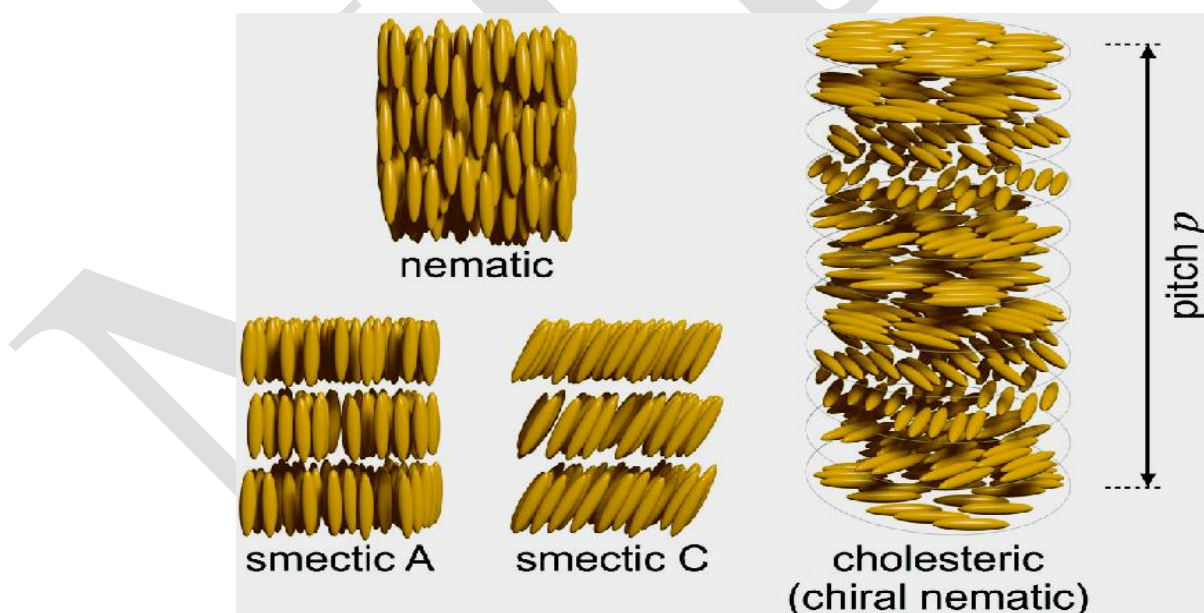
- They are soap like and are clayey or greasy.
- Molecules are cigar shaped.
- These are arranged in layers i.e. have layered structure.
- They do not flow like normal liquids and has limited mobility.
- They have high viscosity.
- Formed at comparatively lower temperature.
- Not affected by external electric or magnetic field.



- Molecules are free to move within the layers but not from one layer to another.
- Flow in layers and difference layers can slide over one another.
- Have short range orientational as well as positional order.
- Are of two types : Smectic A and Smectic C.
- E.g. - Ethyl-p-azoxyphenetole.

c) **Cholesteric Liquid Crystals:** Cholesteric liquid phase is composed of nematic mesogenic molecule containing a chiral centre which produces intermolecular forces that favour alignment between molecules at a slight angle to one another.

- This phase is usually observed from cholesterol derivatives.
- The molecules are essentially chiral.
- The molecules are arranged in layers like Smectic liquid crystals.
- The structure of layers is similar to nematic phase and so it is also known as chiral nematic.
- Each layer in Cholesteric liquid crystal is tilted with respect to the other one, and hence the molecules take a one complete turn of 360 degrees to make a helix.
- The distance covered by the director in making a one complete turn is known as pitch.
- Pitch is inversely proportional to the temperature. It is effected by temperature, pressure and electric & magnetic fields.
- Example: Cholesteryl benzoate (it was the first liquid crystal to be identified).



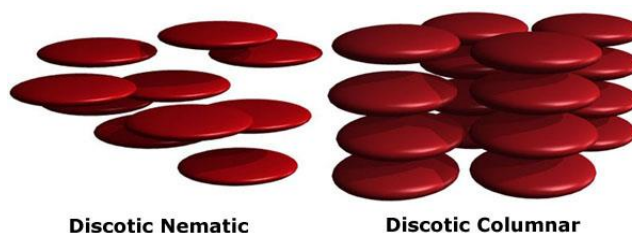
d) **Discotic Liquid Crystals:**

Molecules are essentially disc shaped.

Discotic mesogens are typically composed of an aromatic core surrounded by flexible alkyl chains. The aromatic cores allow charge transfer in the stacking direction through the  $\pi$  conjugate systems. The charge transfer allows the discotic liquid crystals to be electrically semi conductive along the stacking direction.



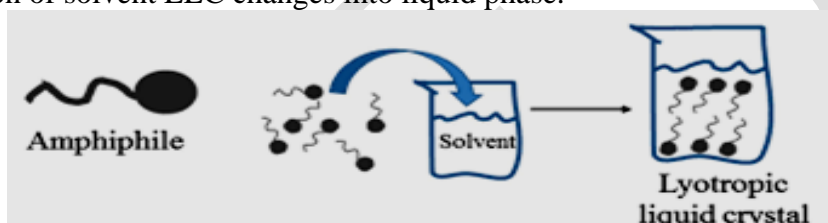
Are of two types:



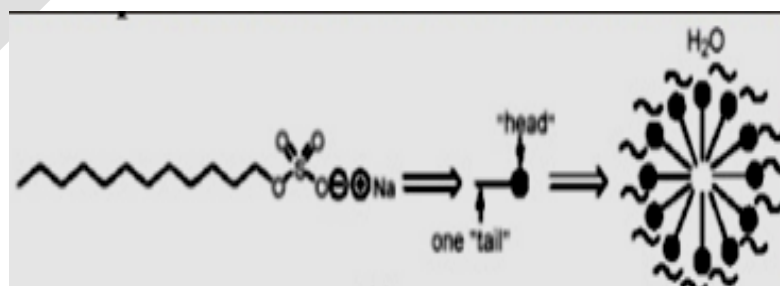
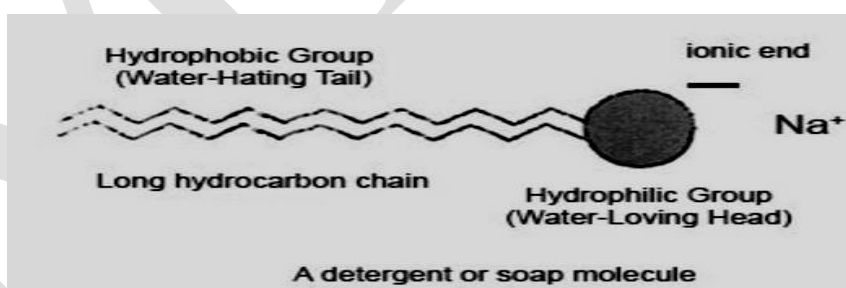
Disc-shaped molecules have a tendency to lie on top of one another forming either discotic nematic phases (with discs oriented similarly) or **columnar** phases (which, obviously, have column-like structure).

## Lyotropic Liquid Crystals:

- These are made on change in the concentration of solvent and/or change in temperature.
- These are solvent and concentration dependent.
- LLC are made by adding solvent to the solid until critical micelle concentration (CMC) is reached. On further addition of solvent LLC changes into liquid phase.



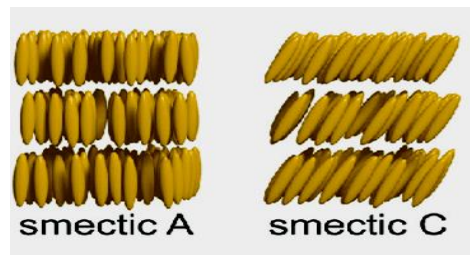
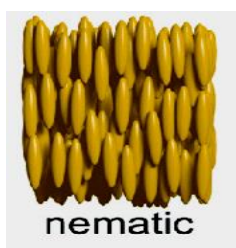
- These are made up of two parts: Hydrophilic polar 'head' and Hydrophobic 'tail', so they are amphiphilic in nature.
- Examples: molecules of soaps, phospholipids (present in cell membranes)



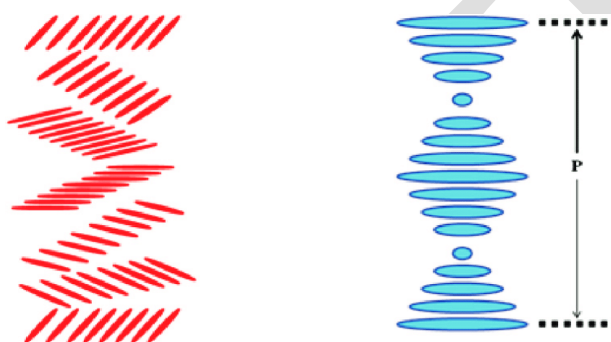
## Applications of liquid crystals:

- Liquid crystals are used for decorative purpose in cosmetics.
- LLC's based delivery system such as cream, ointment; transdermal patches etc have been used in pharmaceutical.
- Thermotropic Cholesteric liquid crystals are used in body care cosmetics.
- Due to their colour effect Cholesteric liquid crystals are used in nail paints, eye shadows etc.
- Discotic liquid crystals are used in photovoltaic devices, organic light emitting diodes (OLED), and molecular wires.
- Liquid crystals are used for displays in LCD's, Calculator, wrist watches etc.
- Cholesteric liquid crystals are used in coloured thermometers.
- Used to locate tumours, veins, arteries, infections, foetal placenta etc.
- Used in research work.
- Used in electronic industries.
- Have Medical applications like localized drug delivery.
- To detect radiations & pollutants in atmosphere.
- Used in non-destructive testing.
- 

	<u>Nematic Liquid Crystals</u>	<u>Smectic Liquid Crystals</u>
1	They are thread like.	They are soap like and are clayey or greasy.
2	Molecules have elongated rod like shape.	Molecules are cigar shaped.
3	Do not have layered structure.	These are arranged in layers i.e. have layered structure.
4	Flow like normal liquids.	They do not flow like normal liquids and has limited mobility.
5	They have low viscosity.	They have high viscosity.
6	Formed at relatively higher temperature.	Formed at comparatively lower temperature.
7	Can be aligned by the application of electric or magnetic field.	Not affected by external electric or magnetic field.
8.	Molecules are free to move in all the directions.	Molecules are free to move within the layers but not from one layer to another.
9.	Flow in all directions & not in layers.	Flow in layers and different layers can slide over one another.
10.	Total loss of positional order but they have orientational order.	Have short range orientational as well as positional order.
11.	E.g.- p-azoxy anisole	E.g. - Ethyl-p-azoxyphenetole.



**Pitch:** Pitch is the property of Cholesteric liquid crystals. It is defined as distance travelled by the director when it gets turned by  $360^\circ$ . It is affected by temperature, pressure and electric & magnetic fields. It is inversely proportional to the temperature. This property of Cholesteric liquid crystals finds the application in coloured thermometers, in nail paints, eye shadows etc.



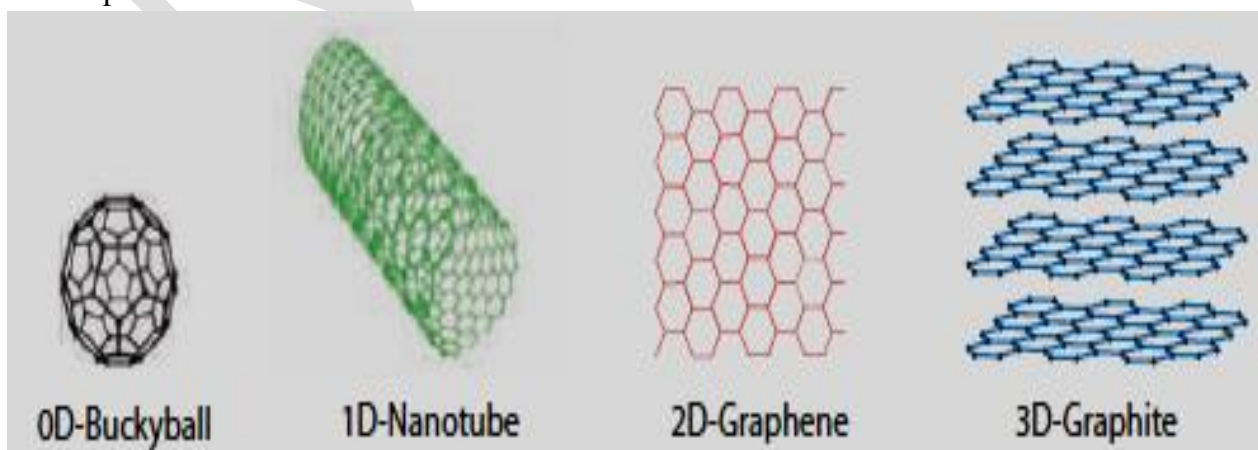
## Nanomaterials

**Nanomaterials:** are materials having at-least one of its dimensions in the nanometre scale ( $1 \text{ nm} = 10^{-9} \text{ m}$ ).

**Nanotechnology:** is the technology of manipulating a material and its properties at the nanoscale (atomic or molecular scale) for target-specific applications.

**Nanostructured materials:** Nanomaterials can be zero, one, two or three dimensional.

- Nanoparticles
- Nanowires
- Nanotubes
- Nanorods
- Nanoporous materials

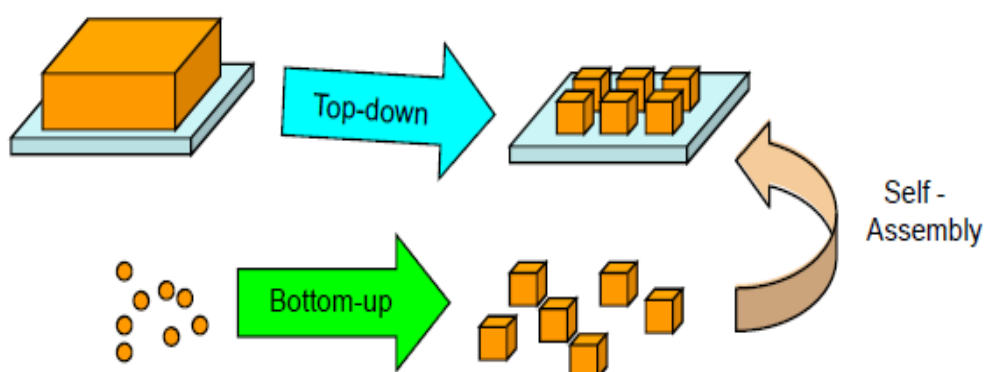


## Effects of Nano size:

- Properties depends on size, composition and structure
- Nano size increases the surface area
- Change in surface energy (higher)
- Change in the electronic properties
- Change in optical band gap
- Change in electrical conductivity
- Higher and specific catalytic activity
- Change thermal and mechanical stabilities
- Different melting and phase transition temperatures
- Change in catalytic and chemical reactivities.

## Nanomaterials synthesis approach:

1. Top down approach: Breaking of bulk material
2. Bottom approach: Buildup of material: Atom→molecule→cluster



## Applications of nanomaterials:

In major view nanomaterials has found their applications in many major areas:

- Electronics
- Medicine
- Engineering and technology
- Industries
- Environment
- Sensors
- Catalysis
- Nanotransistors, Field effect transistors
- Field emission
- Scanning probes in STM
- MEMS devices

- Hydrogen storage
- Energy production , storage and conversion devices
- Nano medicine, drug delivery systems, disease diagnosis
- Chemical , bio, pressure, thermal sensors
- Magnetic materials
- Giant magnetic resistance materials
- Nano machining
- Nano devices
- Nanolithography
- Magnetic storage disk materials
- Thermoelectric materials
- Piezoelectric materials
- Nano electrodes