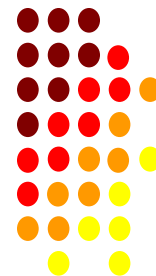


DR. A.P.J. ABDUL KALAM TECHNICAL UNIVERSITY, LUCKNOW



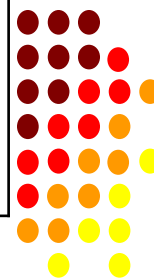
**ENGINEERING- CHEMISTRY (BAS- 102/ 202)
B. TECH. I YEAR**



ENGINEERING CHEMISTRY- B.TECH- FIRST YEAR

SYLLABUS

| Unit | Topics | Lectures |
|------|---|----------|
| I | <p>Atomic and Molecular Structure: Molecular orbital's of diatomic molecules, Bond Order, Magnetic characters and numerical problems. Chemistry of Advanced Materials:</p> <p>Liquid Crystals; Introduction, Types and Applications of liquid crystals, Industrially important materials used as liquid crystals. Graphite and Fullerene; Introduction, Structure and applications.</p> <p>Nanomaterials; Introduction, Preparation, characteristics of nanomaterials and applications of nanomaterials, Carbon Nano Tubes (CNT),</p> <p>Green Chemistry: Introduction, 12 principles and importance of green Synthesis, Green Chemicals, Synthesis of typical organic compounds by conventional and Green route (Adipic acid and Paracetamol), Environmental impact of Green chemistry on society.</p> | 8 |



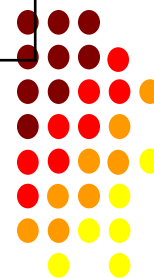
| | | |
|---|--|--|
| <p style="text-align: center;">II</p> | <p>Spectroscopic techniques and Applications: Elementary idea and simple applications of UV, IR and NMR, Numerical problems, Optical isomerism in compounds without chiral carbon, Geometrical isomerism, Chiral Drugs.</p> | <p style="text-align: center;">10</p> |
| <p style="text-align: center;">III</p> | <p>Electrochemistry and Batteries: Basic concepts of electrochemistry. Batteries; Classification and applications of Primary Cells (Dry Cell) and Secondary Cells (Lead Acid battery). Corrosion: Introduction to corrosion, Types of corrosion, Cause of corrosion, Corrosion prevention and control, Corrosion issues in specific industries (Power generation, Chemical processing industry, Oil & gas industry and Pulp & paper industries). Chemistry of Engineering Materials: Cement; Constituents, manufacturing, hardening and setting, deterioration of cement, Plaster of Paris (POP). .</p> | <p style="text-align: center;">8</p> |



| Unit | Topics | Lectures |
|------|---|----------|
| IV | <p>Water Technology: Sources and impurities of water, Hardness of water, Boiler troubles, Techniques for water softening (Lime-Soda, Zeolite, Ion Exchange and Reverse Osmosis process), Determination of Hardness and alkalinity, Numerical problems.</p> <p>Fuels and Combustion: Definition, Classification, Characteristics of a good fuel, Calorific Values, Gross & Net calorific value, Determination of calorific value by Bomb Calorimeter, Theoretical calculation of calorific value by Dulong's method, Ranking of Coal, Analysis of coal by Proximate and Ultimate analysis method, Numerical problems, Chemistry of Biogas production from organic waste materials and their environmental impact on society.</p> | 7 |



| | | |
|---|--|---|
| V | <p>Materials Chemistry: Polymers; Classification, Polymerization processes, Thermosetting and Thermoplastic Polymers, Polymer Blends and Composites, Conducting and Biodegradable polymers, Preparation, properties, industrial applications of Teflon, Lucite, Bakelite, Kelvar, Dacron, Thiokol, Nylon, Buna-N and Buna-S and their environmental impact on society, Speciality polymers.</p> <p>Organometallic Compounds: General methods of preparation and applications of Organometallic compounds (RMgX and LiAlH₄).</p> | 7 |
|---|--|---|



COURSE OUTCOMES

| | |
|--------------|--|
| CO- 1 | Get an understanding of the theoretical principles of chemistry of molecular structure, bonding and properties, Chemistry of advanced materials (liquid crystals, Nanomaterials, Graphite & Fullerene) as well as the Principles of Green Chemistry. |
| CO-2 | Apply the fundamental concepts of determination of structure with various spectral techniques and stereochemistry. |
| CO- 3 | Utilize the theory of construction of electrodes, batteries and fuel cells in redesigning new engineering products and categorize the reasons for corrosion and study methods to control corrosion and develop understanding of Chemistry of Engineering materials (Cement). |
| CO 4 | Develop understanding of the sources, impurities and hardness of water, apply the concepts of determination of calorific values and analyze the coal. |
| CO- 5 | Develop the understanding of Chemical structure of polymers and its effect on their various properties when used as engineering materials. Understanding the applications of specific polymers and Chemistry applicable in industrial process. |



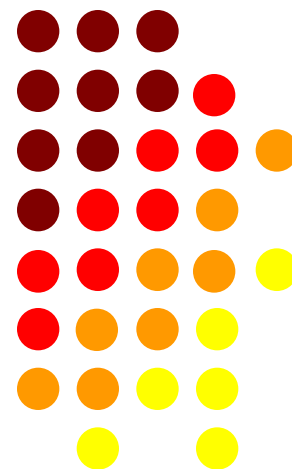
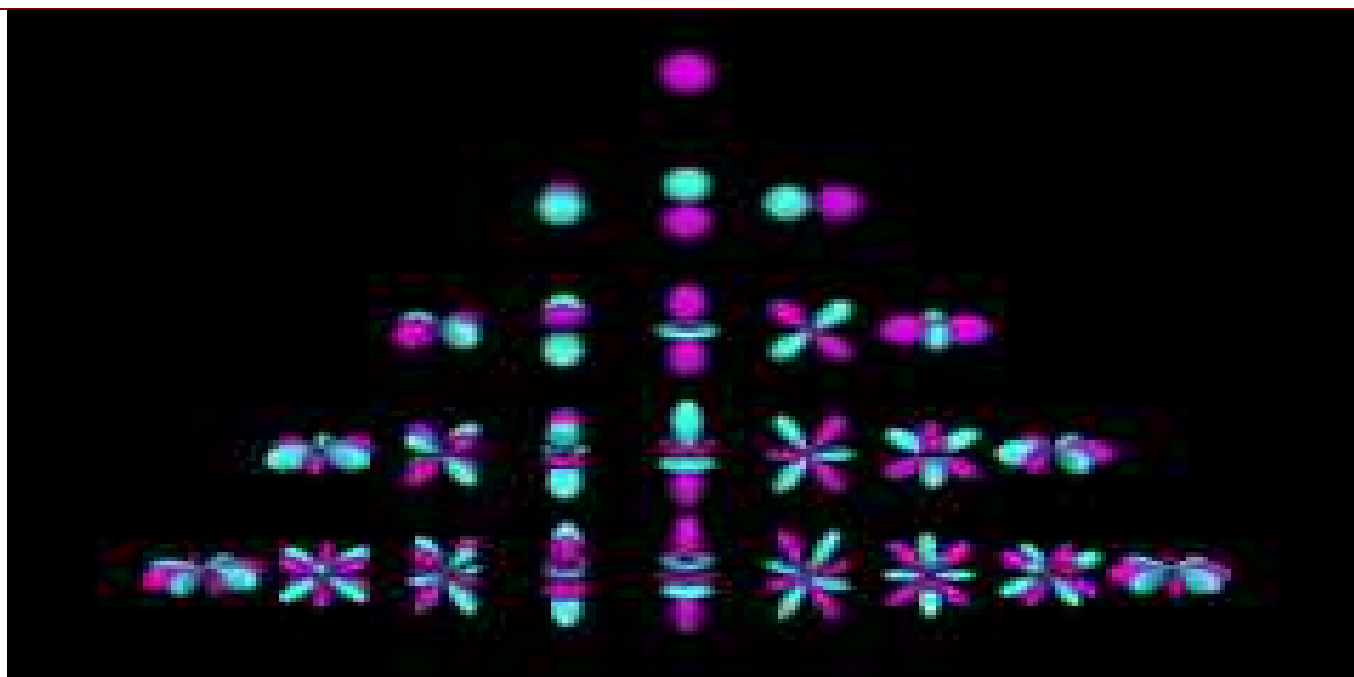
Contents

- **Molecular orbital theory: Introduction and Postulates.**
- **Molecular orbital theory and its applications to homo-nuclear diatomic molecules**
- **Molecular orbital theory and its applications to hetero-nuclear diatomic molecules**
- **Band theory of solids & its applications to Metals**
- **Liquid crystals: Classification, properties and applications**
- **Point defects in Solids: Zero Dimensional defects**
- **Structure and applications of Graphite and fullerenes**
- **Concepts, Properties & Applications of Nano-Science & Nano-materials**



LECTURE 1

MOLECULAR ORBITAL THEORY INTRODUCTION AND POSTULATES



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)***

i. If ψ_A & ψ_B are wave functions of atoms A & B then according to LCAO: $\psi_{M.O} = \psi_A \pm \psi_B$



ii. Two types of molecular orbitals are formed: bonding and anti bonding molecular orbitals.

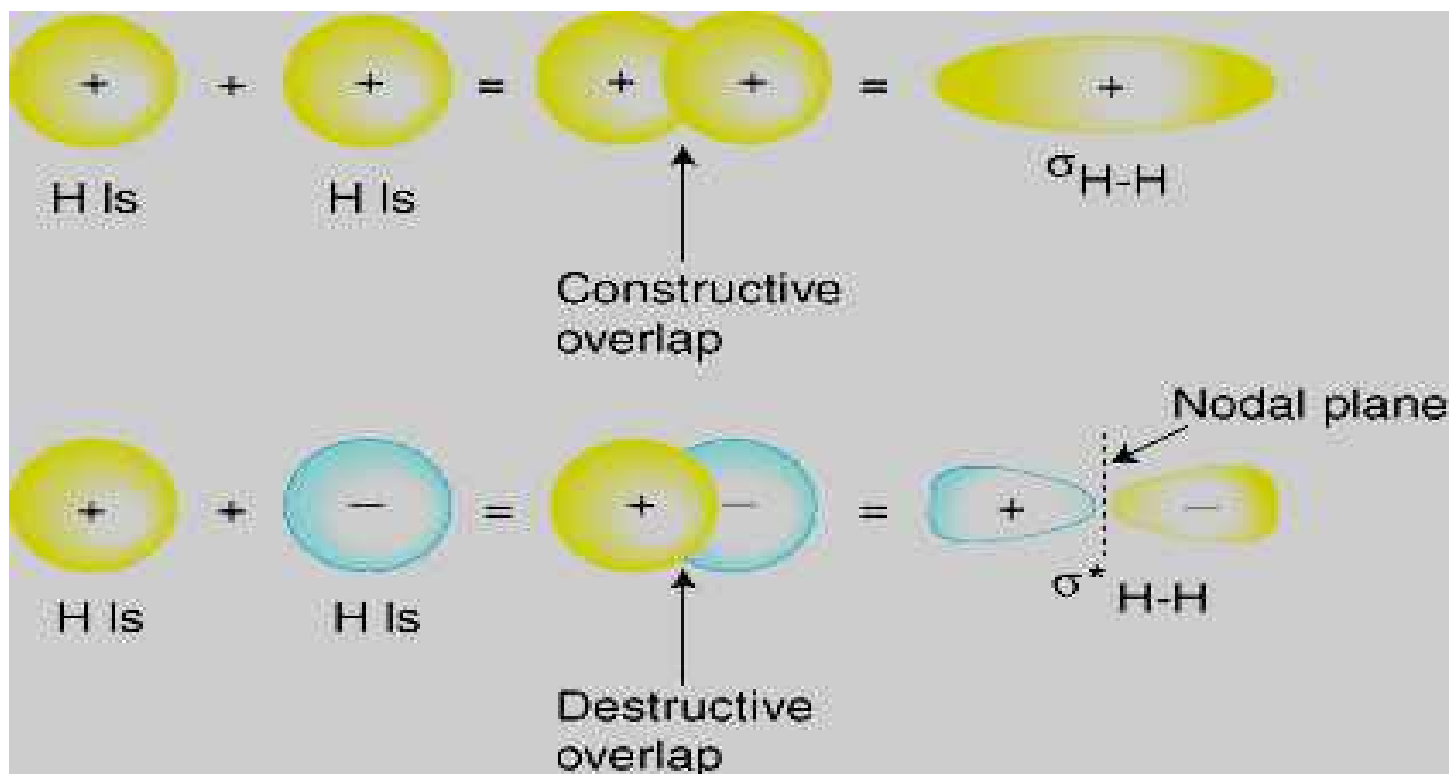
iii. Molecular orbitals formed the *additive overlap* of two atomic wave functions is known as *Bonding Molecular orbital*. i.e. $\Psi_b = \Psi_A + \Psi_B$

iv. Molecular orbitals formed by *subtractive overlap* of two atomic orbitals wave function is called *Anti-bonding molecular orbital* i.e. $\Psi_a = \Psi_A - \Psi_B$



Linear combination of atomic orbitals

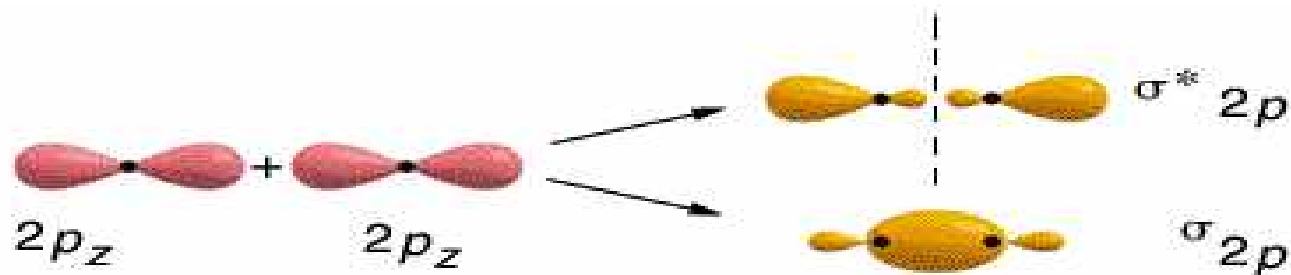
S-orbital linear combination



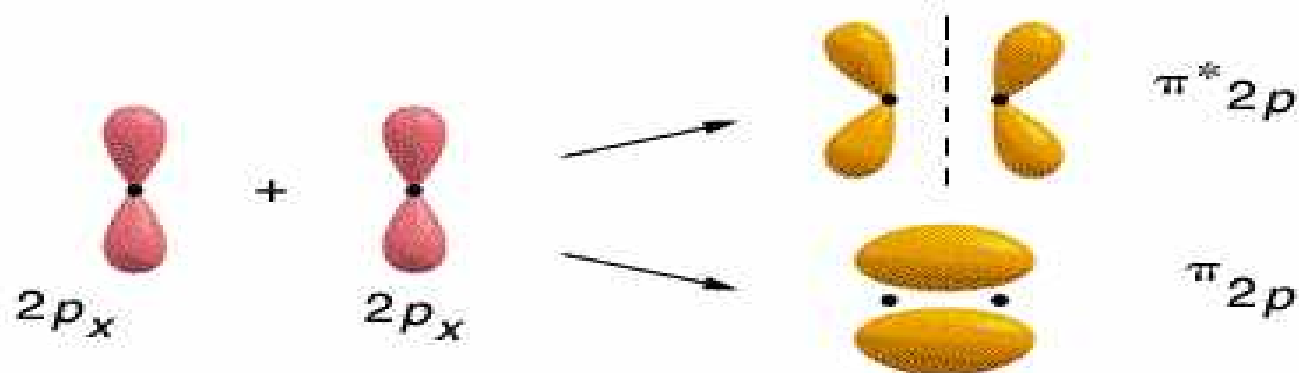
Linear combination of atomic orbitals

P-orbital linear combination

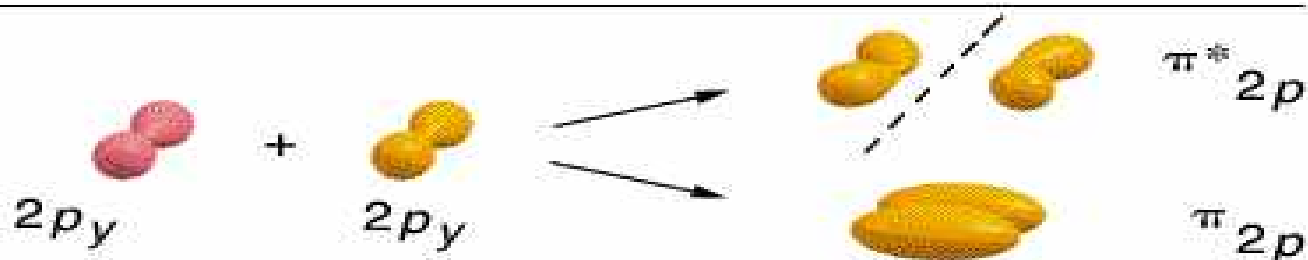
(a)



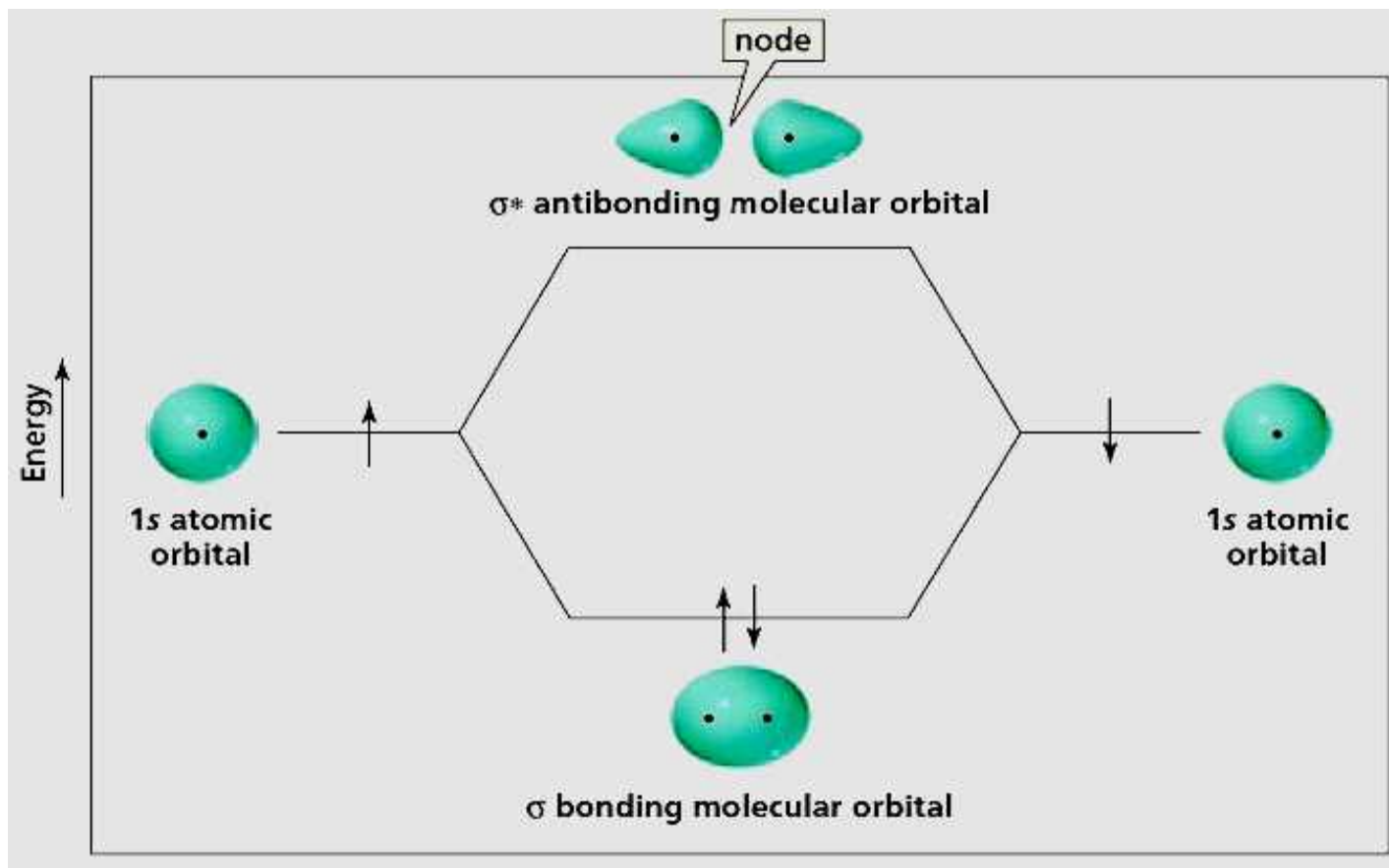
(b)



(c)



2. The no. of molecular orbitals formed is always equal is the number of atomic orbitals taking part in bond formation.



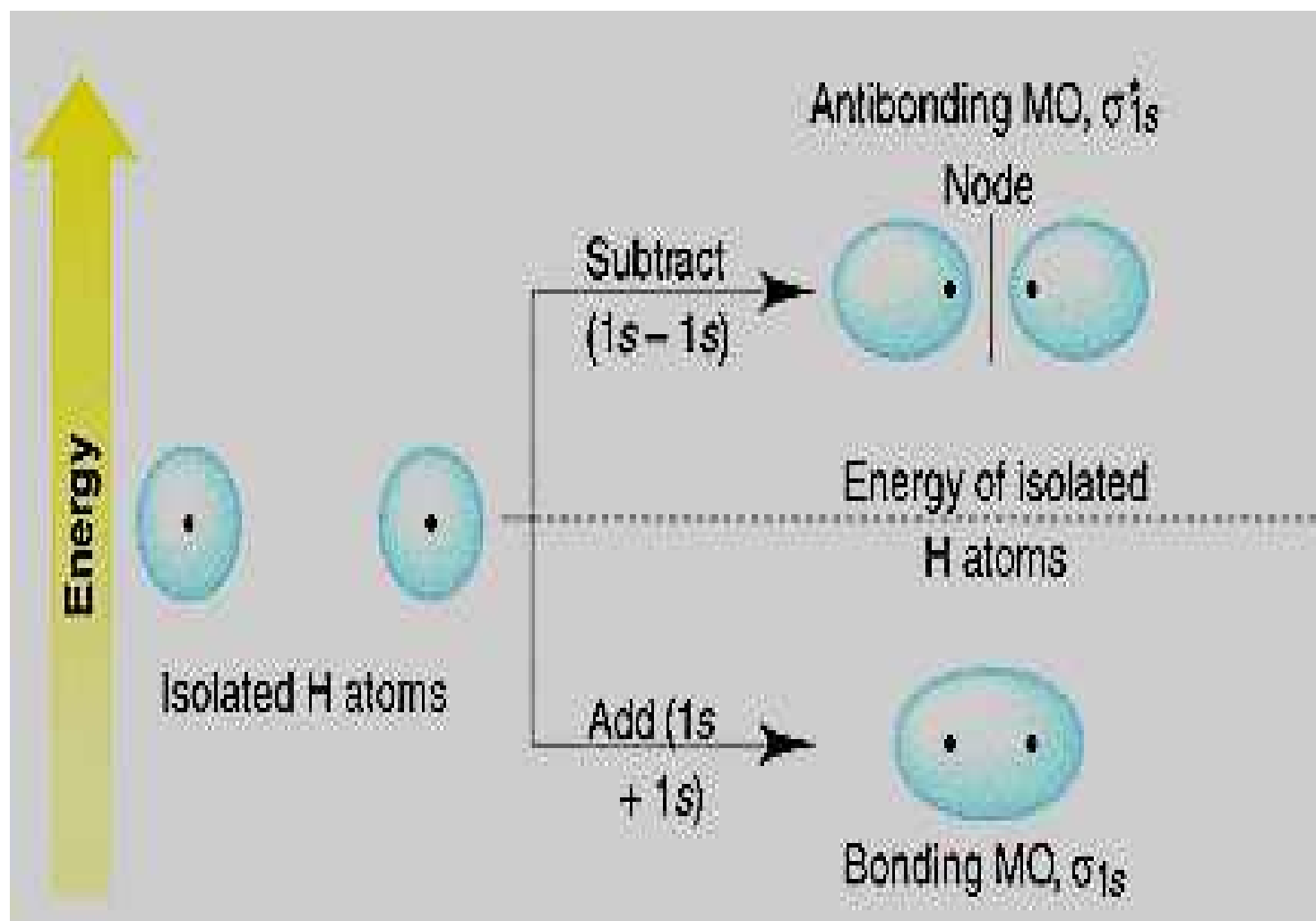
3. Energy level of bonding M.O. is less than that of individual atomic orbitals. So, electrons present in bonding M.O stabilizes the molecule.

4. Energy level of anti-bonding M.O is more than that of individual atomic orbitals. So electrons 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 is that of individual atomic orbitals.

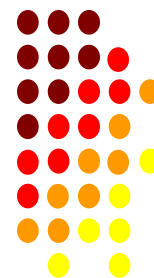
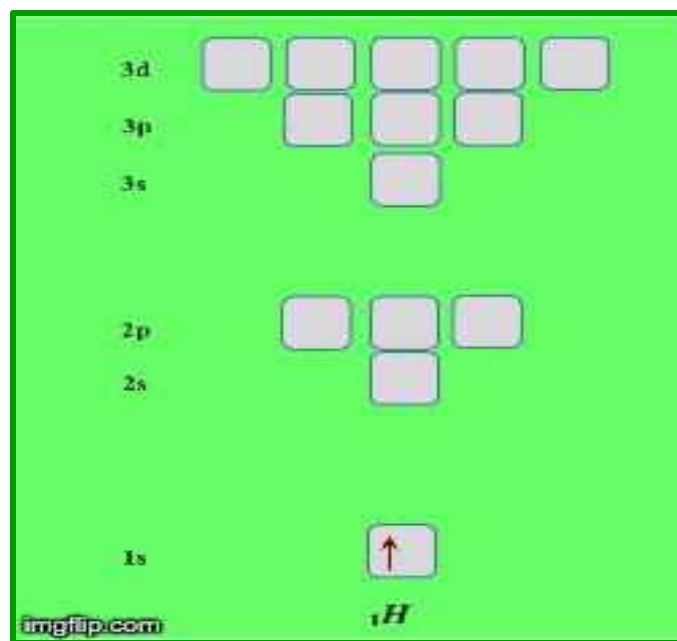
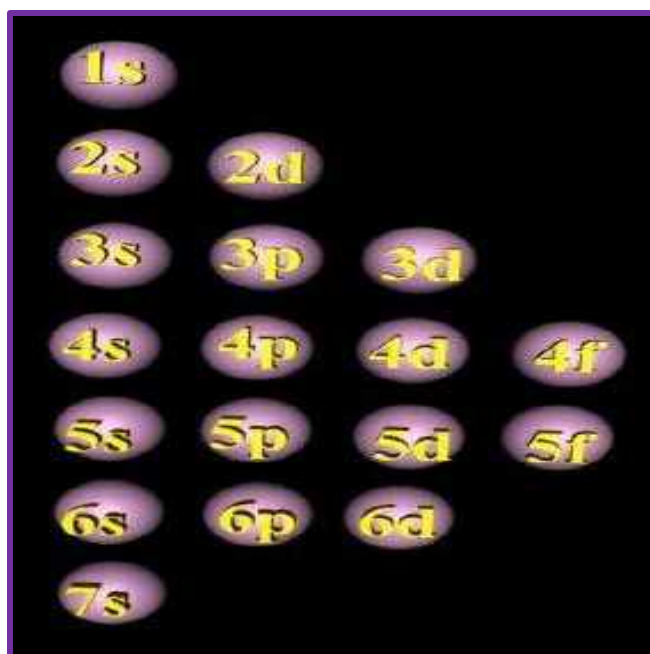
6. Molecular orbitals are *polycentric*.





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* & *Hunds rule of maximum multiplicity*.



9. The electrons are filled in the molecular orbitals according to the following order:

From H₂ to N₂:

$\sigma_{1s}, \sigma^*_{1s}, \sigma_{2s}, \sigma^*_{2s}, \pi_{2px} = \pi_{2py}, \sigma_{2pz}, \pi^*_{2px} = \pi^*_{2py}, \sigma^*_{2pz}$

From O₂ to Ne₂:

$\sigma_{1s}, \sigma^*_{1s}, \sigma_{2s}, \sigma^*_{2s}, \sigma_{2pz}, \pi_{2px} = \pi_{2py}, \pi^*_{2px} = \pi^*_{2py}, \sigma^*_{2pz}$

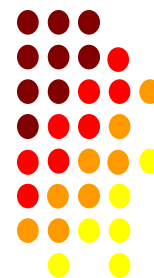


- 10.** Molecules or ions with *one or more unpaired e⁻* in molecular orbitals are *paramagnetic* while those with all paired electrons in M.O. are called *diamagnetic*.
- 11.** Stability & strength of a chemical bond is expressed in terms of bond order.
- 12. Bond Order** – Bond order is equal to one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



Significance of bond order:

- Zero B.O.: Molecule 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.
- ***Bond order \propto Bond stability \propto 1/ Bond length***



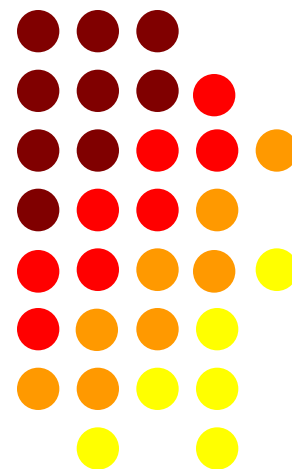
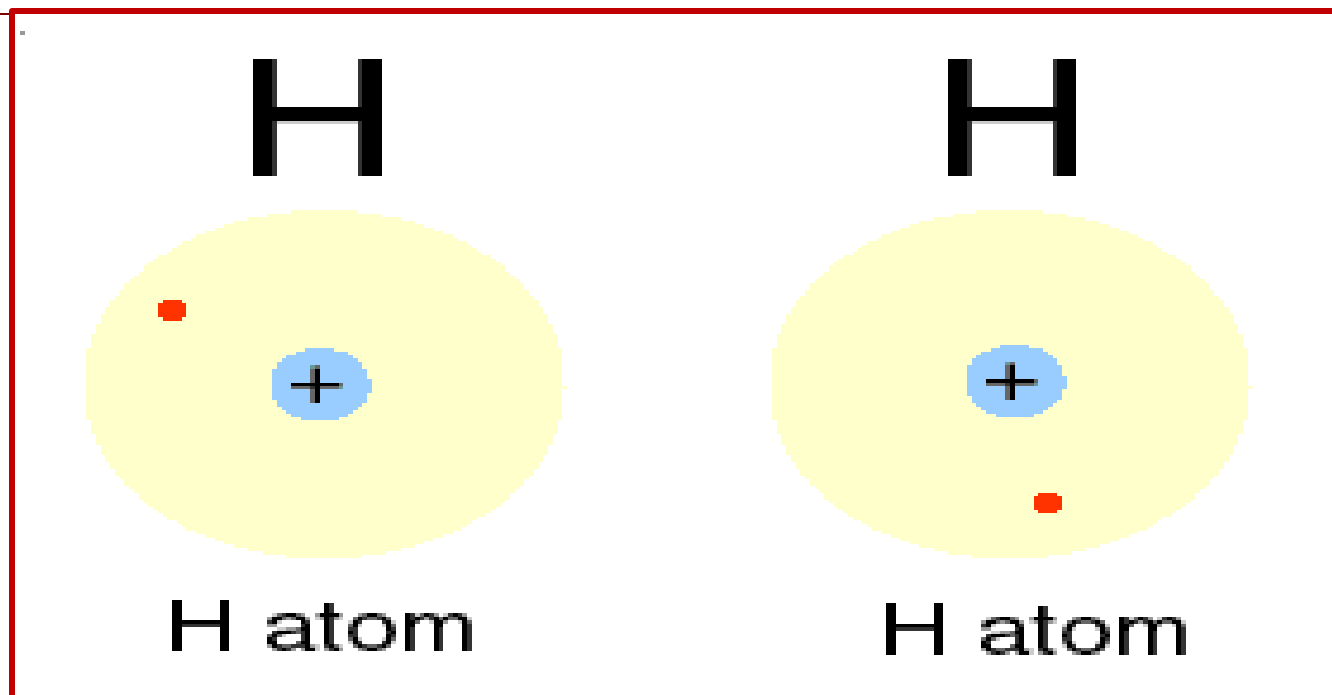
Differences between bonding and antibonding molecular orbitals.

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



LECTURE - 2

Application of Molecular orbital theory to Homo-nuclear diatomic molecules



Molecular Orbital Diagrams of some homo-diatomic molecules

HOMODIATOMIC MOLECULES: These are the molecules formed of same atoms. Example: O_2 , H_2 etc. Following order of configuration is followed for various molecules:

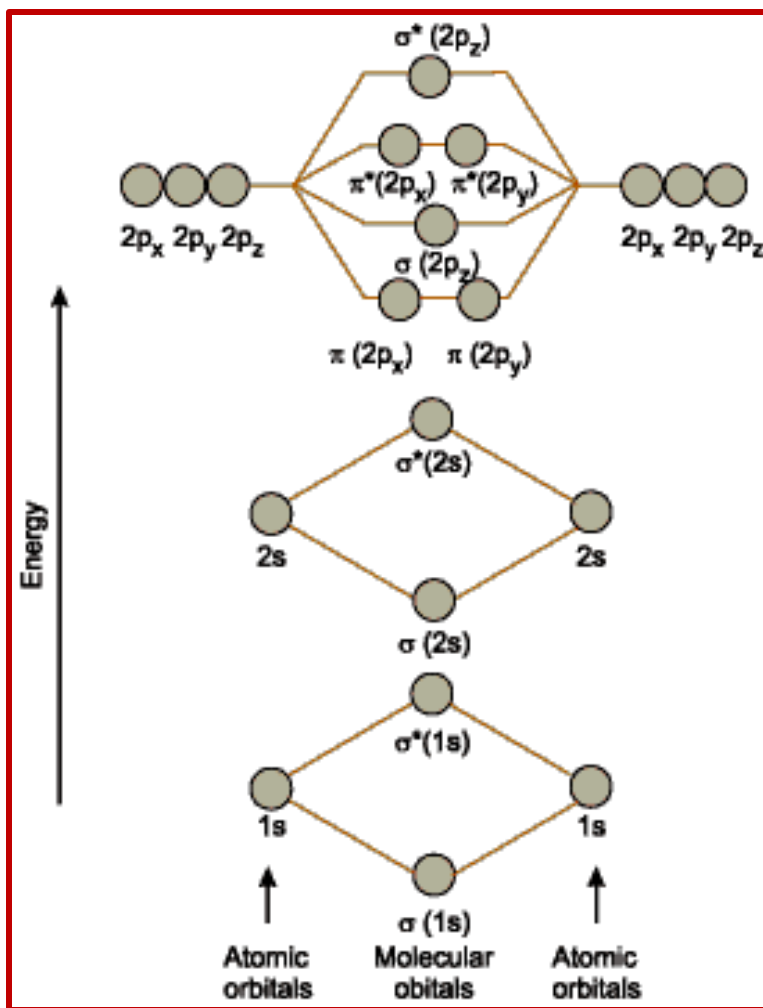
From H_2 to N_2 :

σ_{1s} , σ^*_{1s} , σ_{2s} , σ^*_{2s} , $\pi_{2px} = \pi_{2py}$, σ_{2pz} , $\pi^*_{2px} = \pi^*_{2py}$, σ^*_{2pz}

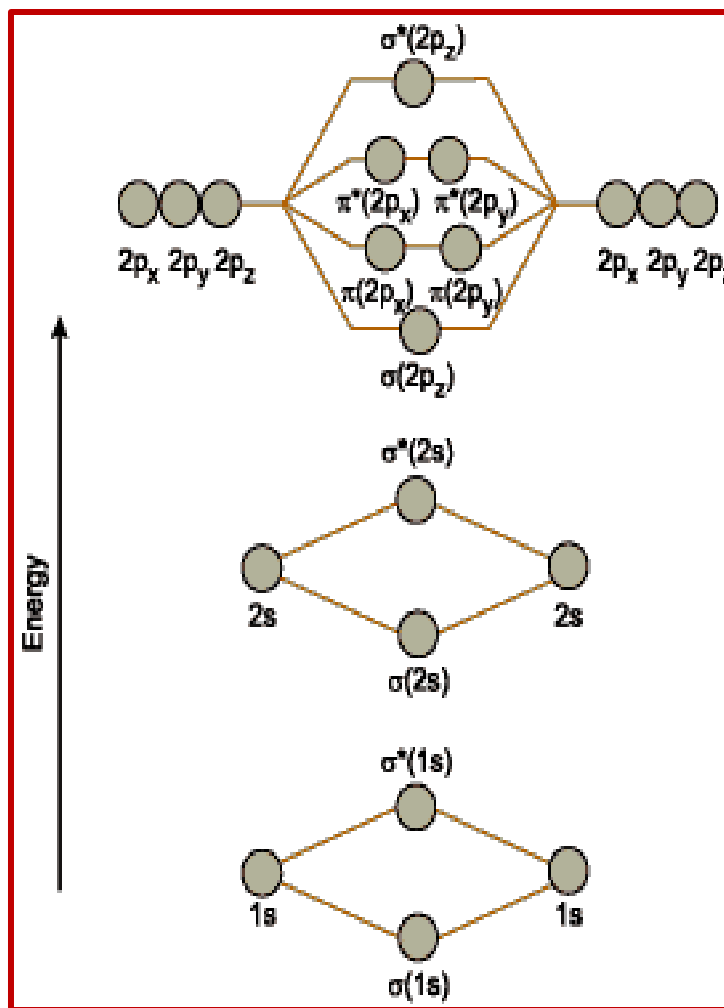
From O_2 to Ne_2 :

σ_{1s} , σ^*_{1s} , σ_{2s} , σ^*_{2s} , σ_{2pz} , $\pi_{2px} = \pi_{2py}$, $\pi^*_{2px} = \pi^*_{2py}$, σ^*_{2pz}

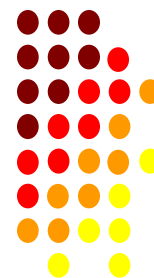




From H_2 to N_2



From O_2 to Ne_2



Hydrogen (H_2) and Hydrogen ion (H_2^+)

Hydrogen (H_2): ($2e^-$): $\sigma 1s^2, \sigma^* 1s^0$

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

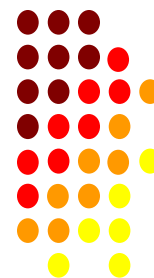
The molecule is **diamagnetic** due to paired electrons.

H_2^+ : $\sigma 1s^{-1}$

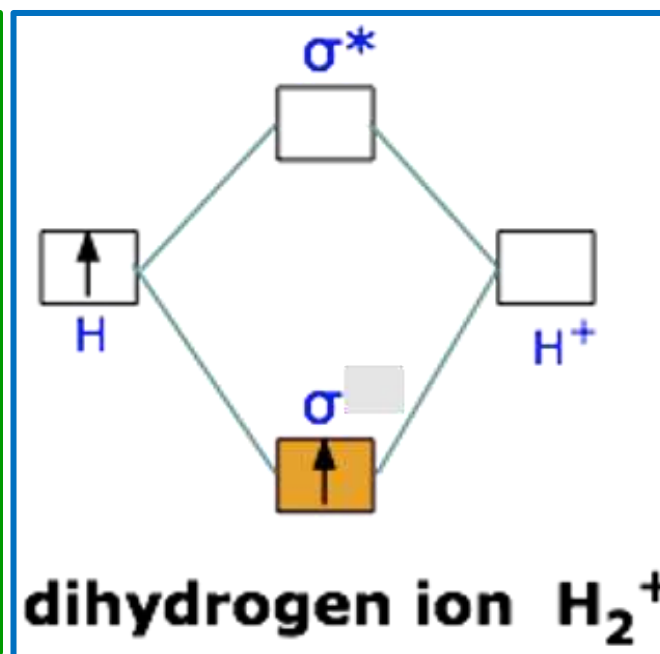
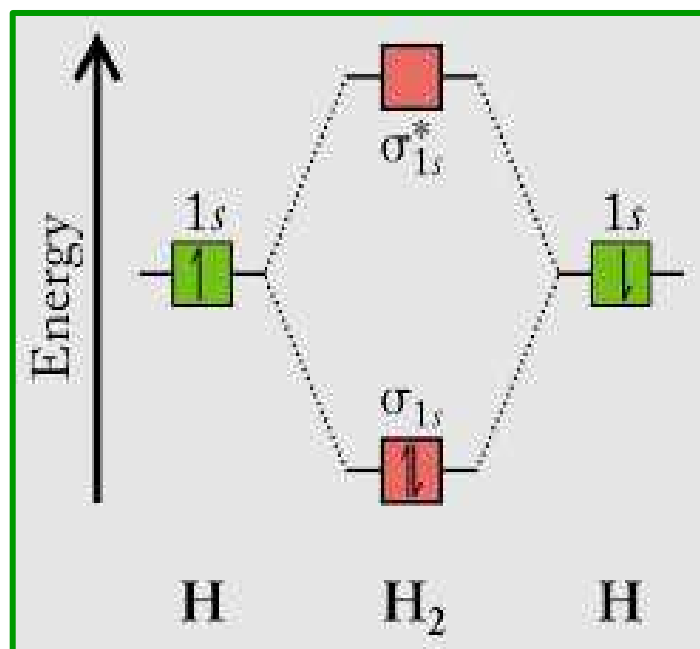
$$B.O. = \frac{1}{2}(N_b - N_a) = \frac{1}{2}(1 - 0) = 0.5$$

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

Paramagnetic due to presence of one unpaired electron



Molecular orbital diagrams of Hydrogen (H_2) and Hydrogen ion (H_2^+)

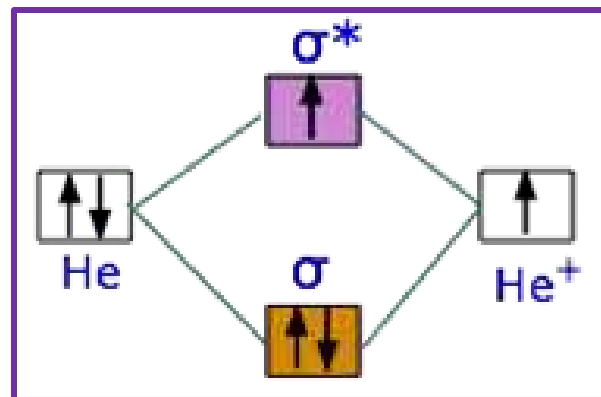


Dihelium (He_2) and dihelium ion (He_2^+)

He_2^+ : ($3e^-$): $\sigma 1s^2$

$$B.O = \frac{1}{2}(N_b - N_a) = \frac{1}{2}(2 - 1) = 0.5$$

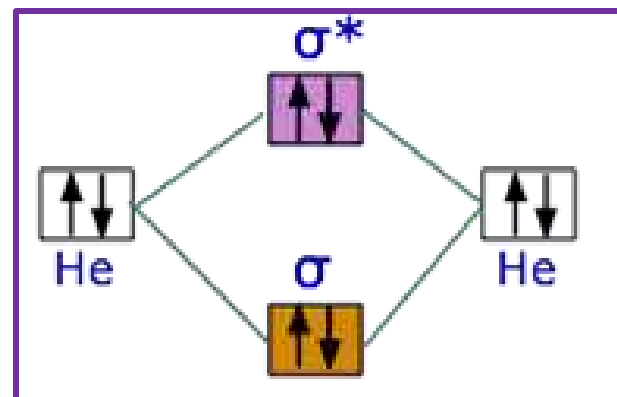
It is paramagnetic in nature



He_2 : ($4e^-$): $\sigma 1s^2, \sigma^* 1s^2$

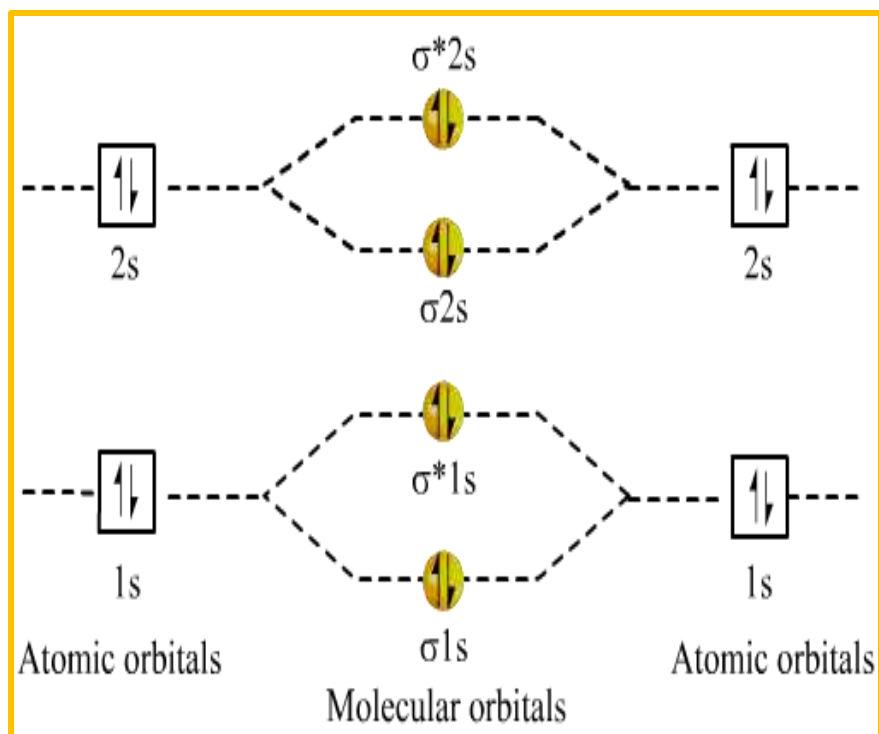
$$B.O = \frac{1}{2}(N_b - N_a) = \frac{1}{2}(2 - 2) = 0$$

He_2 cannot exist as its bond order is zero, So **Helium exists in mono atomic form (He)**.



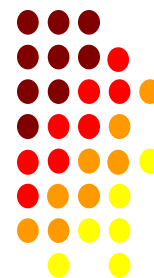
Be₂ does not exist in nature:

Be₂ (8e⁻): $\sigma 1s^2$, $\sigma^* 1s^2$, $\sigma 2s^2$, $\sigma^* 2s^2$



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

As the bond order of Be₂ is zero, the molecule cannot be formed. So, ***it exists in mono atomic form (Be).***



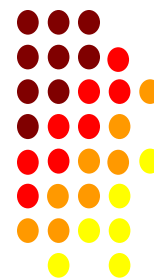
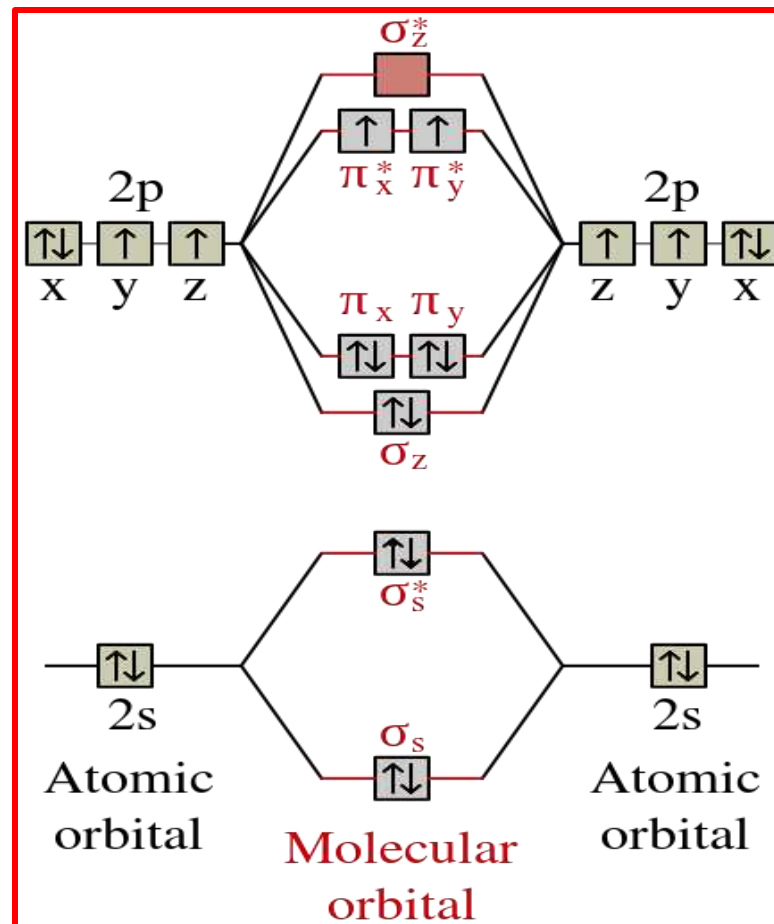
O₂ (16e⁻):

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

$$\begin{aligned} B.O. &= \frac{1}{2}(N_b - N_a) \\ &= \frac{1}{2}(8 - 4) \\ &= \frac{1}{2} \times 4 = 2 \end{aligned}$$

Magnetic Behaviour:

Paramagnetic due to presence of two unpaired electrons in the molecular orbitals.

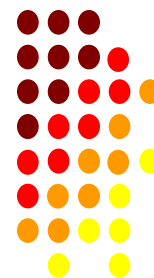
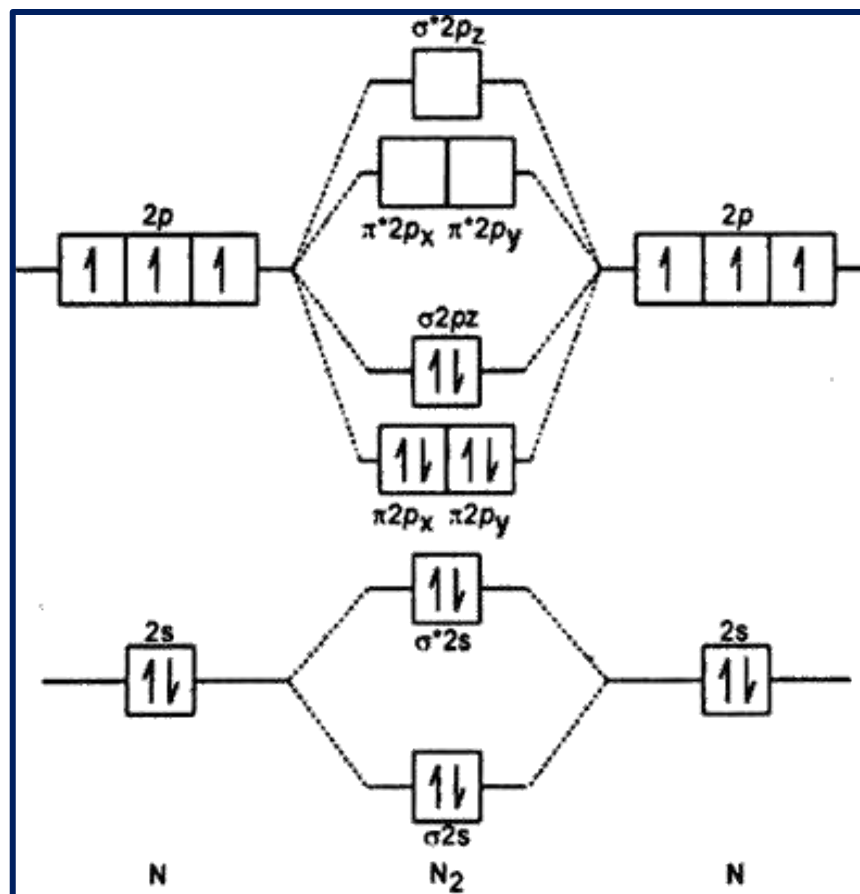


N₂ (14e⁻):

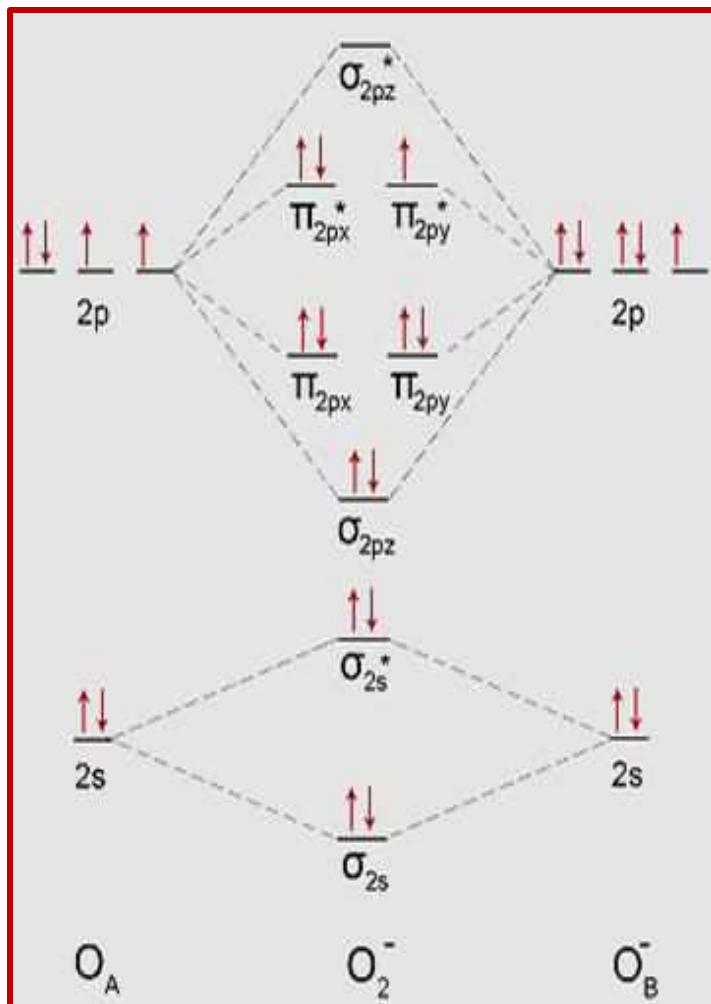
$$\begin{aligned}
 \text{B.O.} &= \frac{1}{2}(N_b - N_a) \\
 &= \frac{1}{2}(8 - 2) \\
 &= \frac{1}{2} \times 6 = 3
 \end{aligned}$$

Magnetic

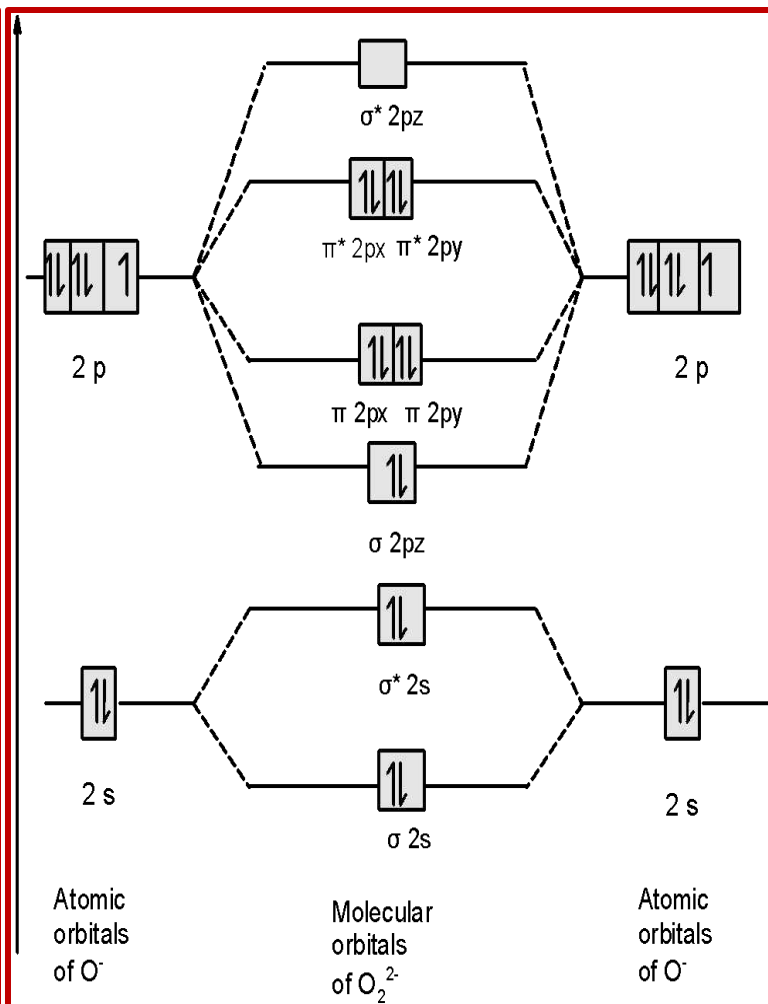
Behaviour: It is **diamagnetic** in nature since all the electrons in molecular orbitals are paired.



Superoxide (O_2^-) and peroxide (O_2^{2-}) ions



Paramagnetic



Diamagnetic



$$\text{B.O. of } \text{O}_2 = \frac{1}{2} (N_b - N_a) = \frac{1}{2} (8 - 4) = 2$$

$$\text{B.O. of } \text{O}_2^- = \frac{1}{2} (N_b - N_a) = \frac{1}{2} (8 - 5) = 1.5$$

$$\text{B.O. of } \text{O}_2^{-2} = \frac{1}{2} (N_b - N_a) = \frac{1}{2} (8 - 6) = 1$$

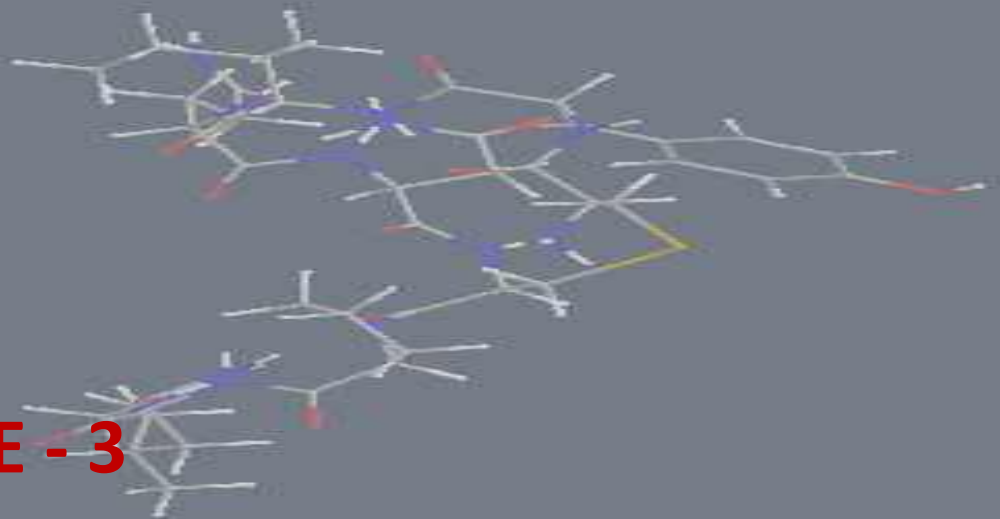
Since, ***B.O. \propto stability.***

So, the order of stability will be: $\text{O}_2 > \text{O}_2^- > \text{O}_2^{-2}$

Also, ***B.O. \propto 1 / Bond Length***

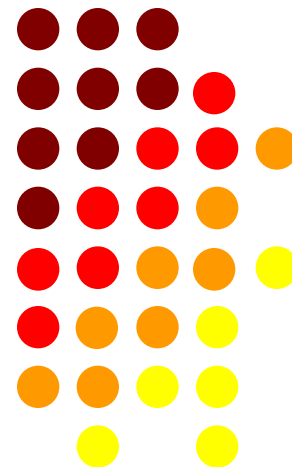
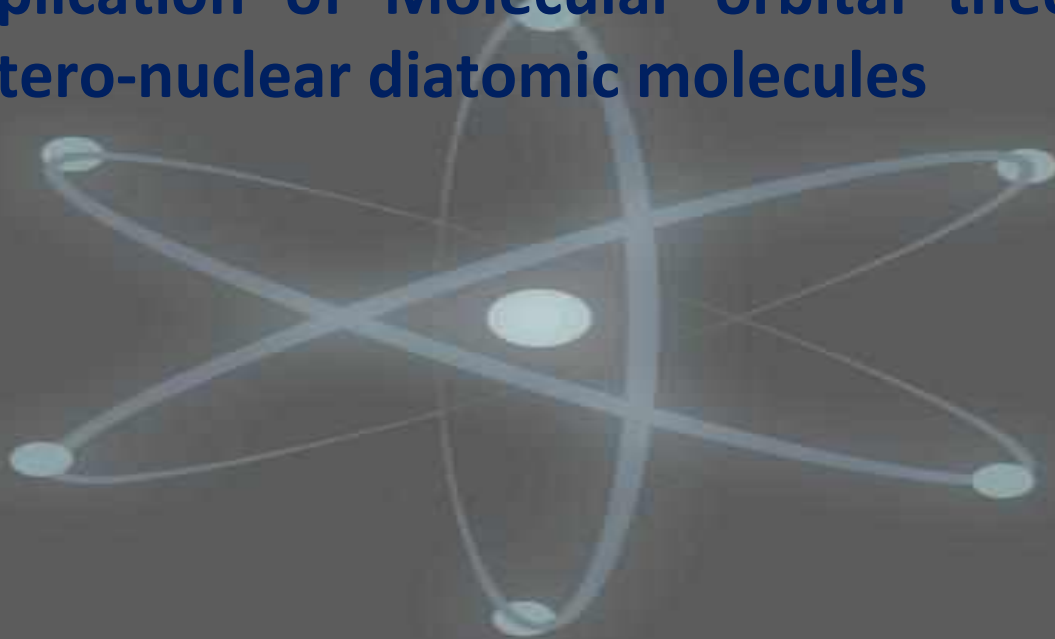
So, the order of bond length will be: $\text{O}_2^{-2} > \text{O}_2^- > \text{O}_2$





LECTURE - 3

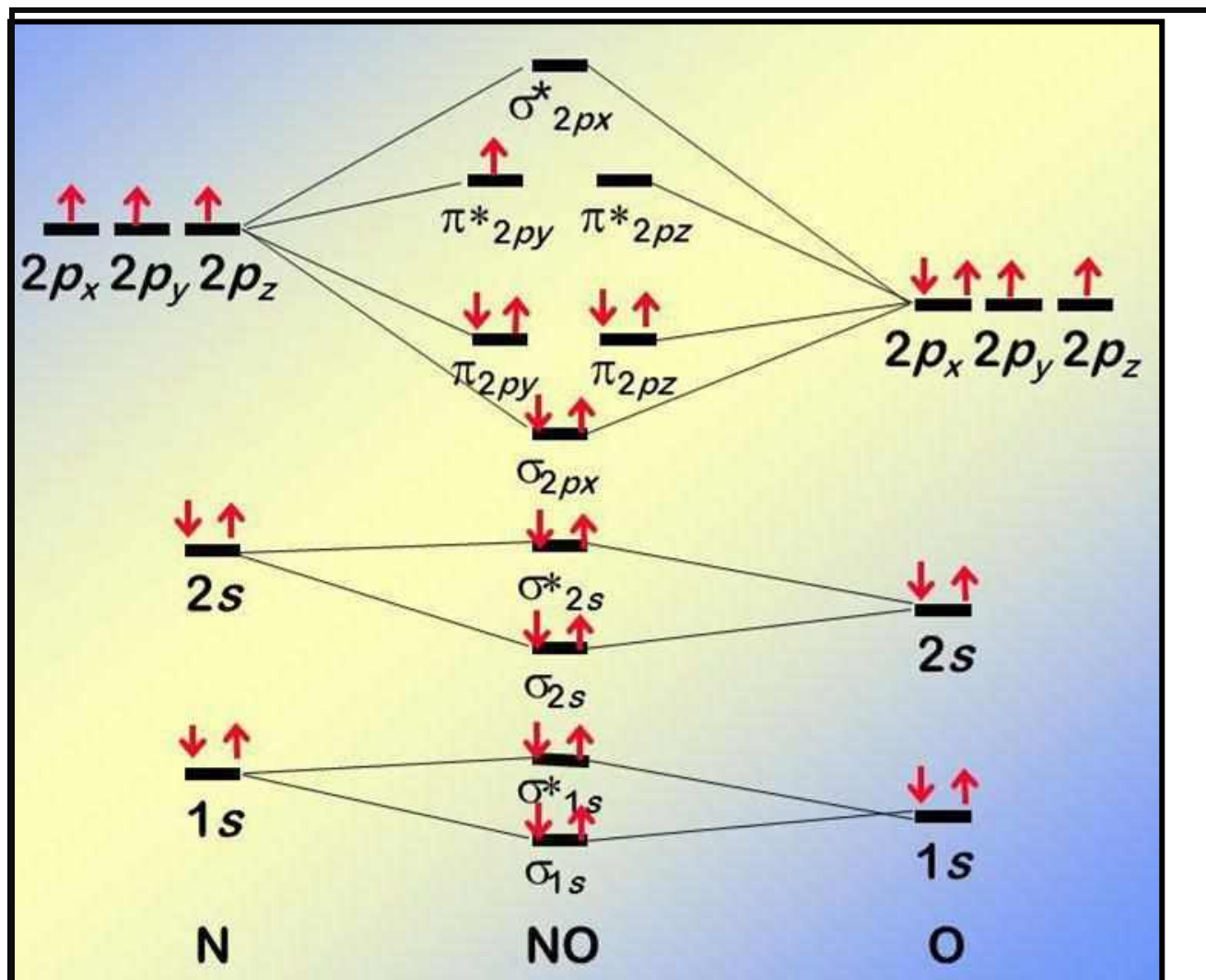
Application of Molecular orbital theory to Hetero-nuclear diatomic molecules



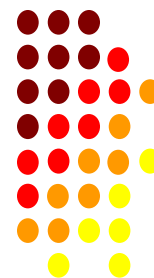
Hetero-diatomic molecules

- Molecules that contain two different atoms.
- Molecular orbital energy level diagram is always skewed towards the more electronegative atom.
- More electronegative atomic orbital lies closer to bonding M.O. and less electronegative atomic orbital lies closer to antibonding M.O.

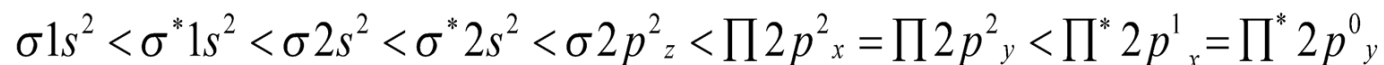




MO Diagram of NO



MO Diagram of NO (15 e⁻):

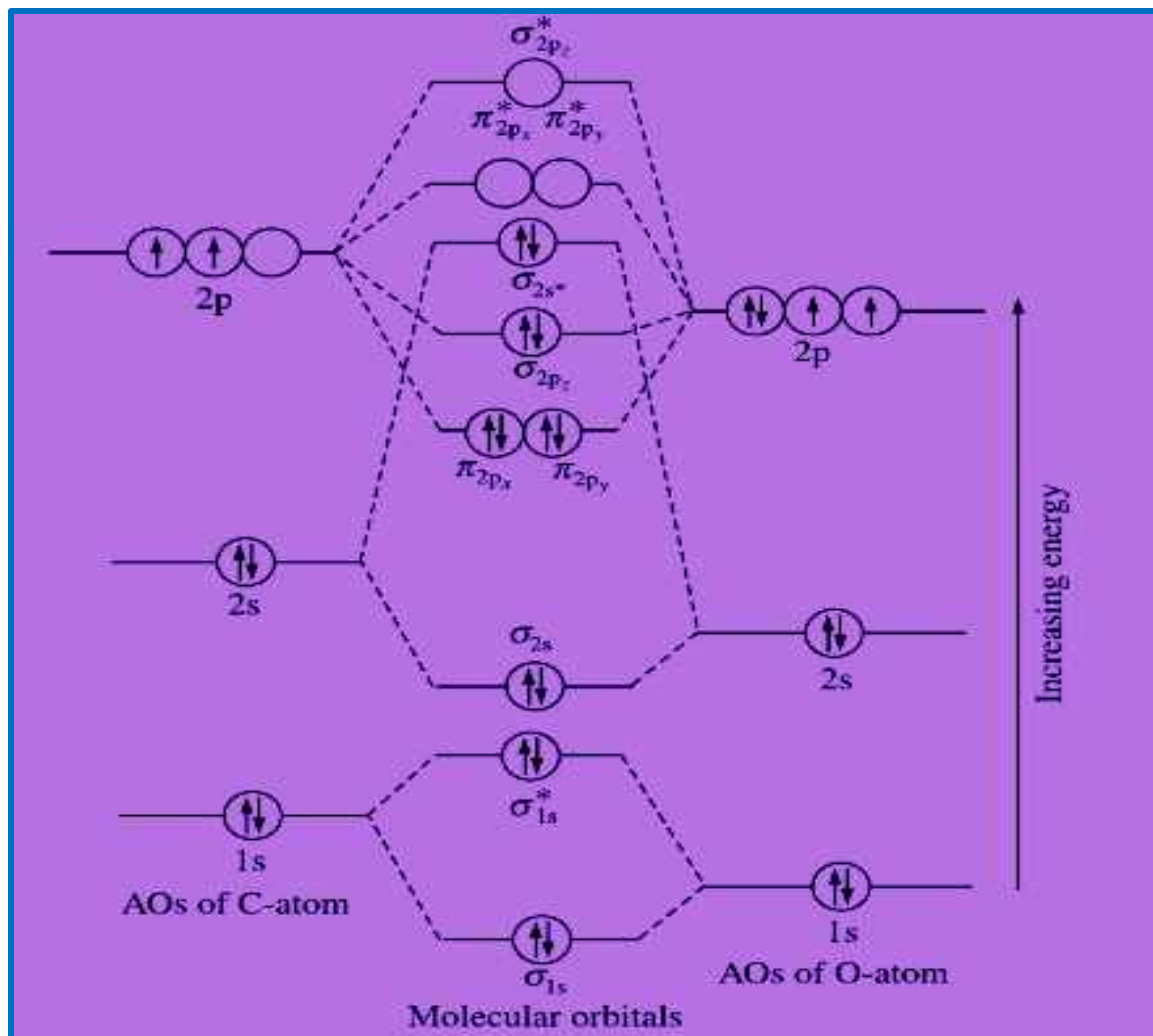


Its bond order is calculated as :

$$\begin{aligned} \text{Bond order} &= \frac{1}{2} [10 - 5] \\ &= \frac{1}{2} [5] = 2.5 \end{aligned}$$

NO molecule is ***paramagnetic*** in nature due to an unpaired electron in $\pi^* 2p_x$ orbital

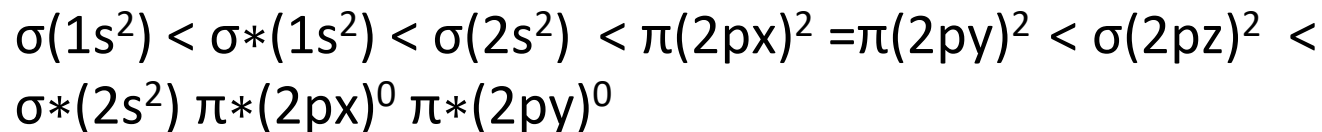




MO Diagram of CO



MO Diagram of CO: (14 e⁻):



Its bond order is calculated as :

$$\begin{aligned} \text{Bond order} &= \frac{1}{2} [10 - 4] \\ &= \frac{1}{2} [6] = 3 \end{aligned}$$

Diamagnetic in behavior as it does not contain any unpaired electron.



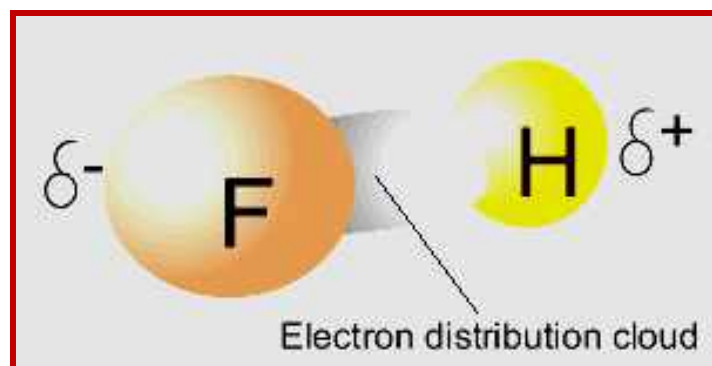
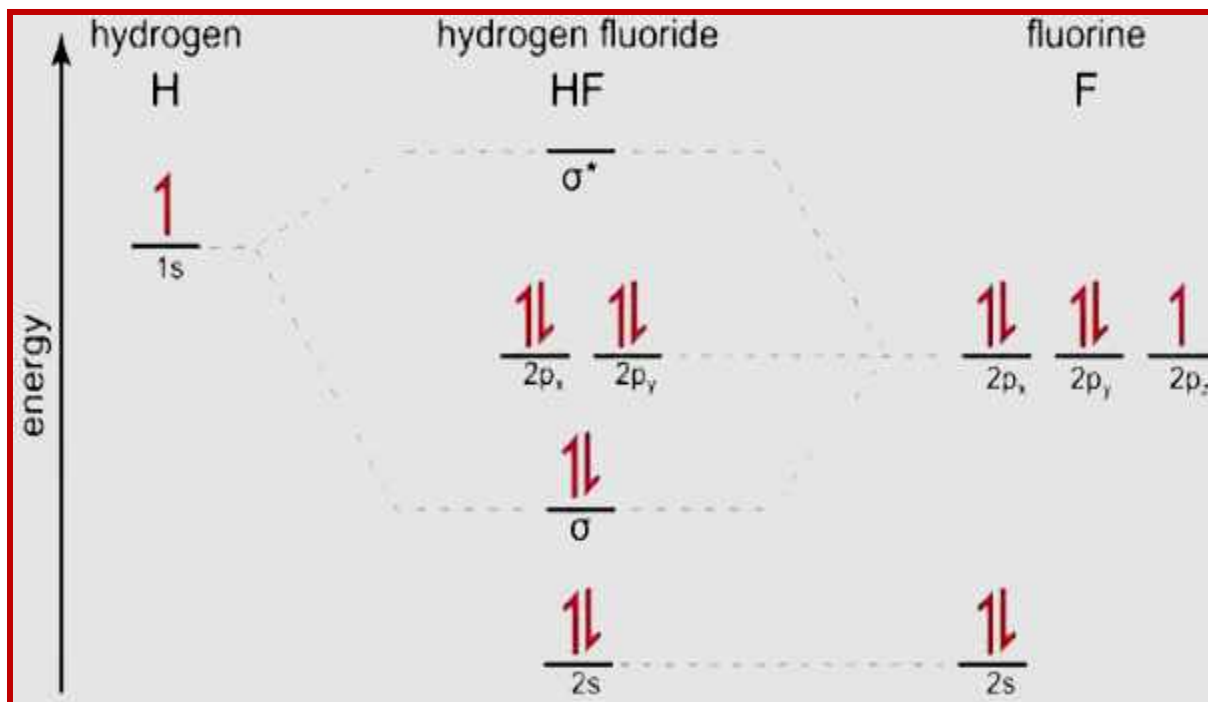
HF (10 e⁻) : σ_{spz}^2

1s and 2s electrons as well as 4 electrons of p orbital of fluorine do not participate in the formation of molecular orbital of HF and exist as lone pairs. 1s of hydrogen pairs up with 2p unpaired electron of fluorine to form σ_{spz} molecular orbital.

$$\begin{aligned} B.O. \text{ of } HF &= \frac{1}{2}(N_b - N_a) \\ &= \frac{1}{2}(2 - 0) = 1 \end{aligned}$$

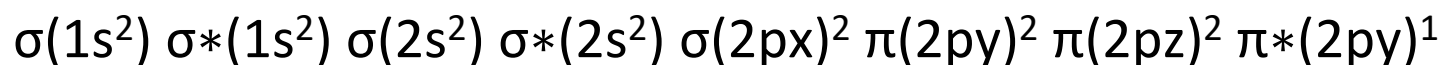
It is a stable molecule as the bond order is 1.
HF is ***diamagnetic*** in nature.





Ques. On the basis of MO theory calculate the bond order of NO. Will NO be paramagnetic or diamagnetic?

Ans. The electronic configuration of NO =



$$\text{Bond order} = \frac{\text{Bonding electron} - \text{non-bonding electron}}{2}$$

$$\text{Bond order} = \frac{10 - 5}{2}$$

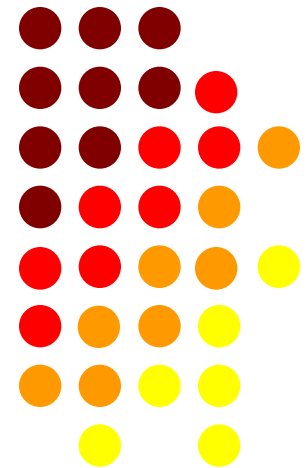
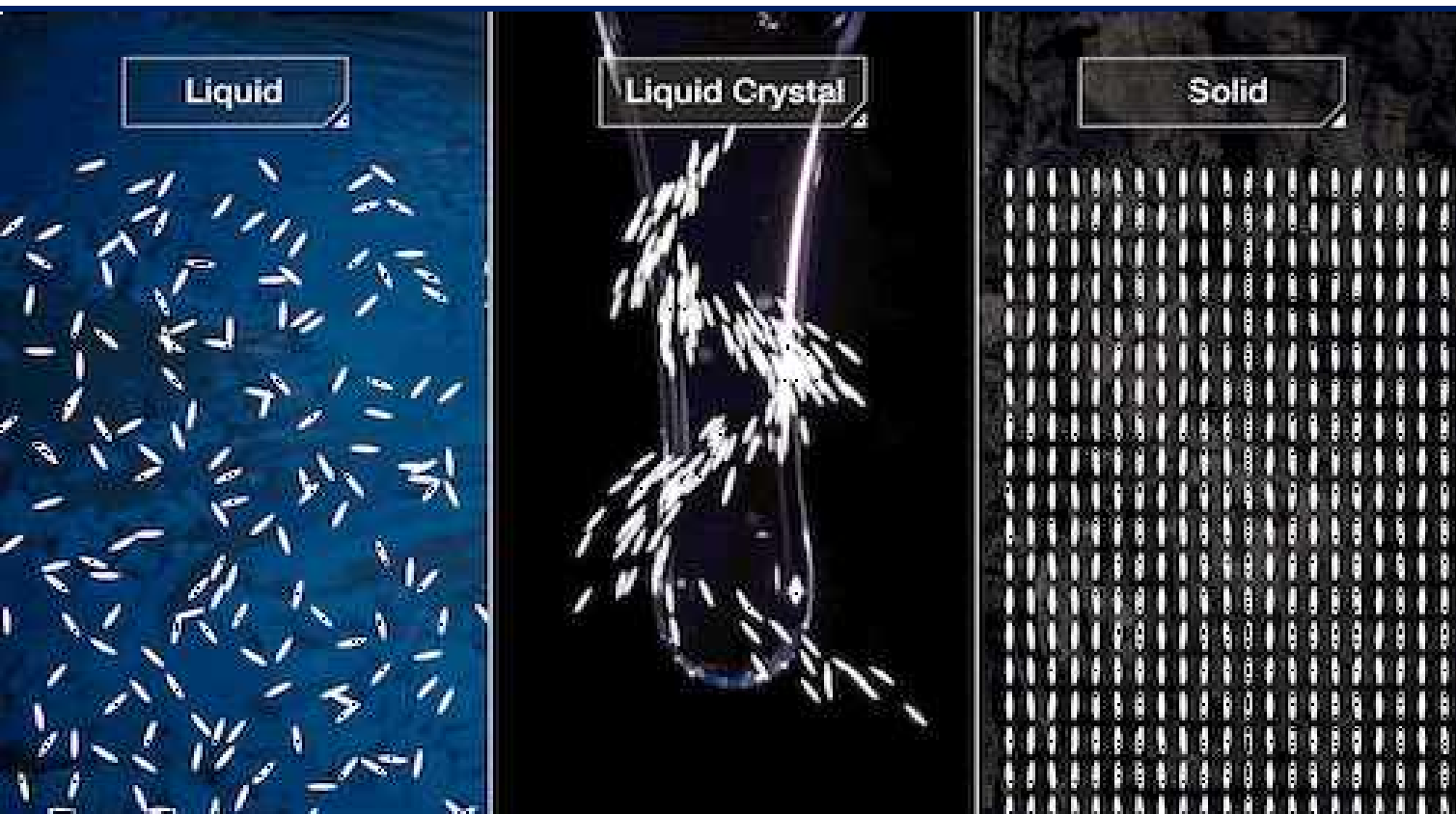
$$\text{Bond order} = 2.5$$

Hence, the bond order of NO will be 2.5.



LECTURE - 4

Liquid crystals: Classification, Properties and Applications



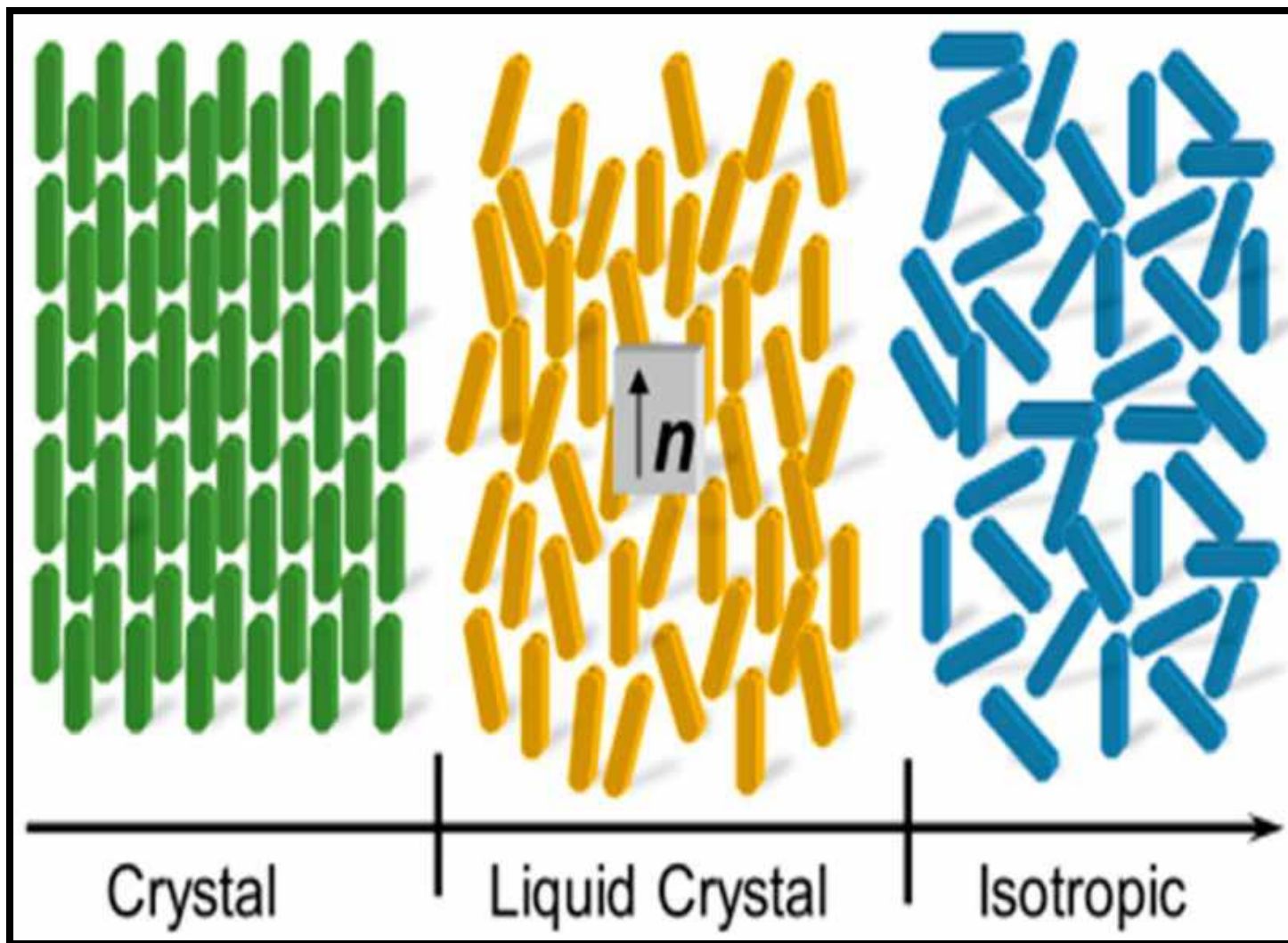
LIQUID CRYSTALS

Liquid Crystals are state of matter which has properties between those of conventional liquids and 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***.

Friedrich Reinitzer, Austrian botanist studied about it first in 1888 in a material known as **cholesteryl benzoate** .





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).

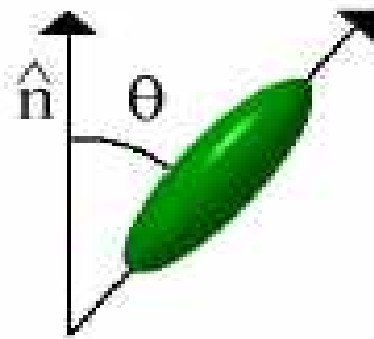
Orientalional order: represents a measure of the tendency of the molecules to align along the director on a long-range basis.



Bond Orientational Order: describes a line joining the centres of nearest neighbour molecules without requiring a regular spacing along that line.

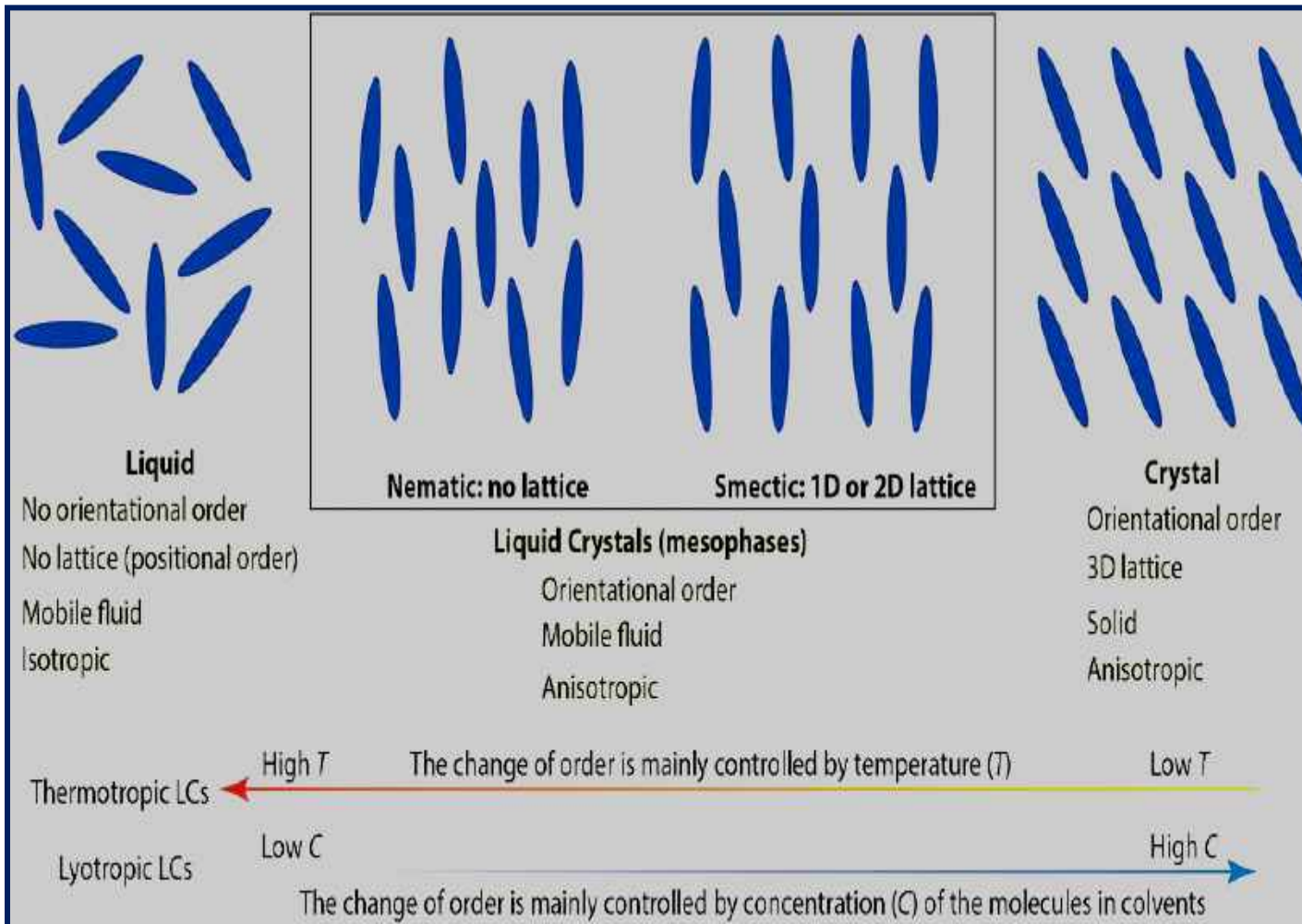
Positional order + Orientational order = crystal phase

Varying Positional order + Orientational order = LC phase



- Positional order + Orientational order =
Crystal Phase
- Positional order + No Orientational order = **Plastic Phase**
- Varying Positional order + Orientational order = **Liquid crystalline Phase**
- No positional order + No Orientational order =
Isotropic (Liquid) Phase





Properties of liquid crystals

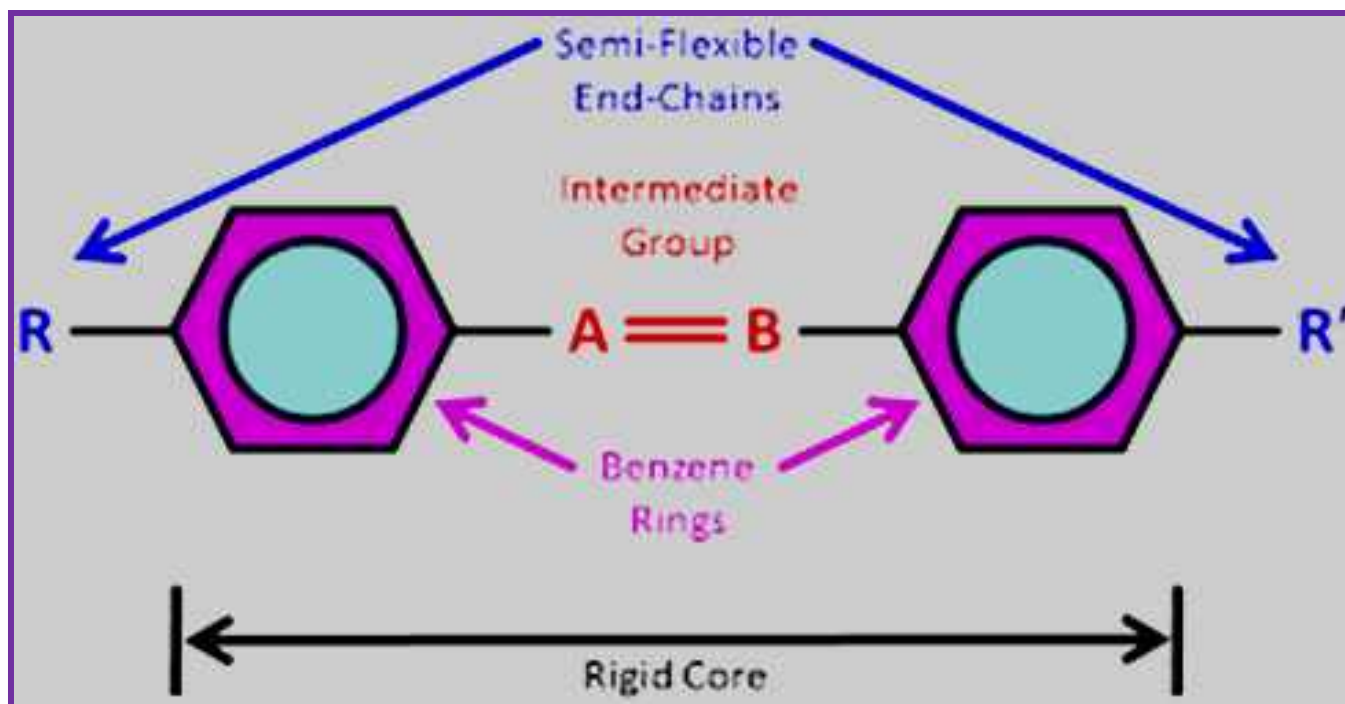
- The molecules are *rod shaped or disc shaped*.
- All liquid crystals are mesogens but all mesogens are not liquid crystals.
- Molecules are *anisotropic* in nature.
- Assuming that the direction of preferred orientation in a liquid crystal (LC) is \uparrow , this direction can be represented by an 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 (***π - π interaction***).
- A typical Liquid Crystal molecule is represented by ***a central rigid part***, known as ***mesogen*** (generally aromatic) and the ***flexible ends*** (generally aliphatic groups).



- It consists of *two or more ring systems connected by a central linkage group*.

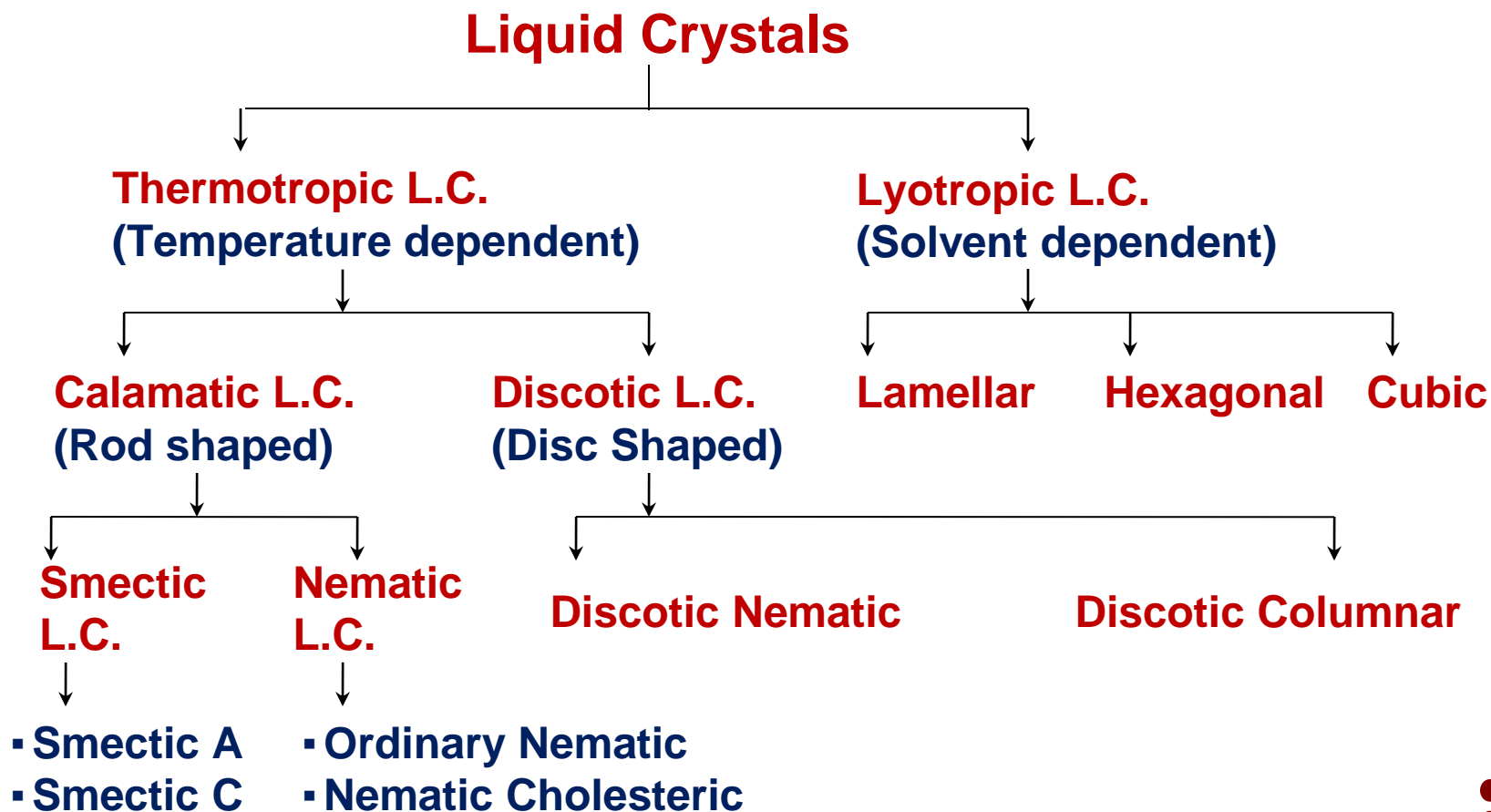


Essential requirements for a molecule to be a liquid crystal

- 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*.
- Although LC's combine the properties of a crystalline solid and an isotropic liquid, they exhibit very specific electro-optical phenomena, which have no equivalent analogues in solids or in liquids.

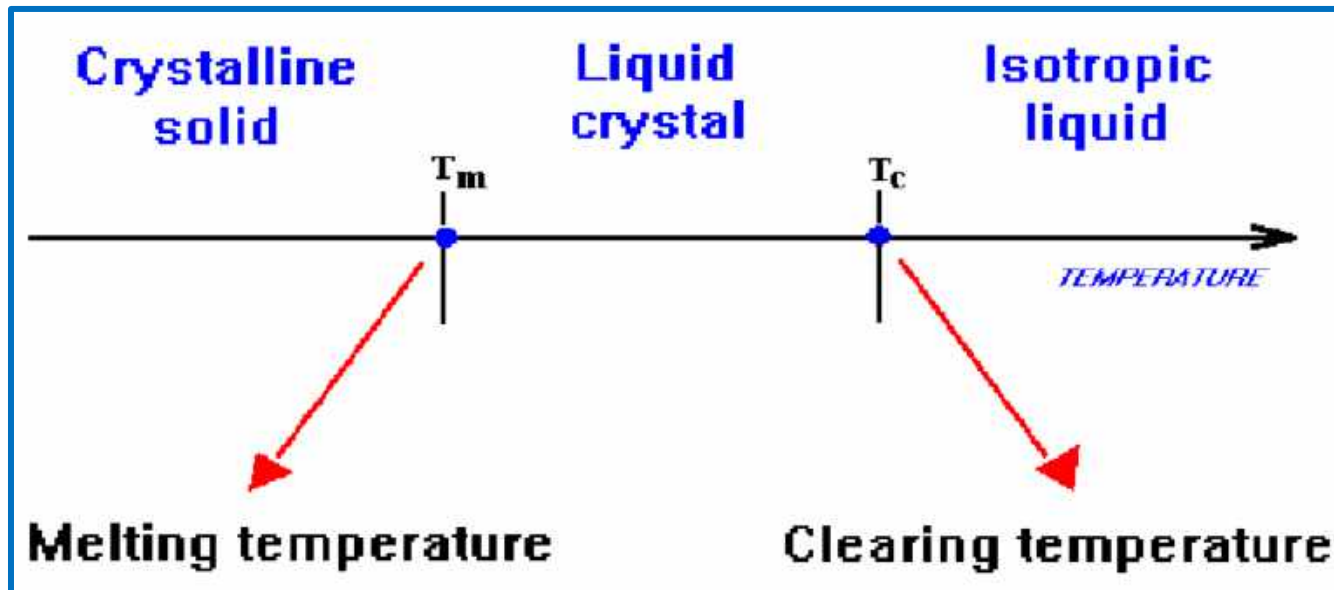


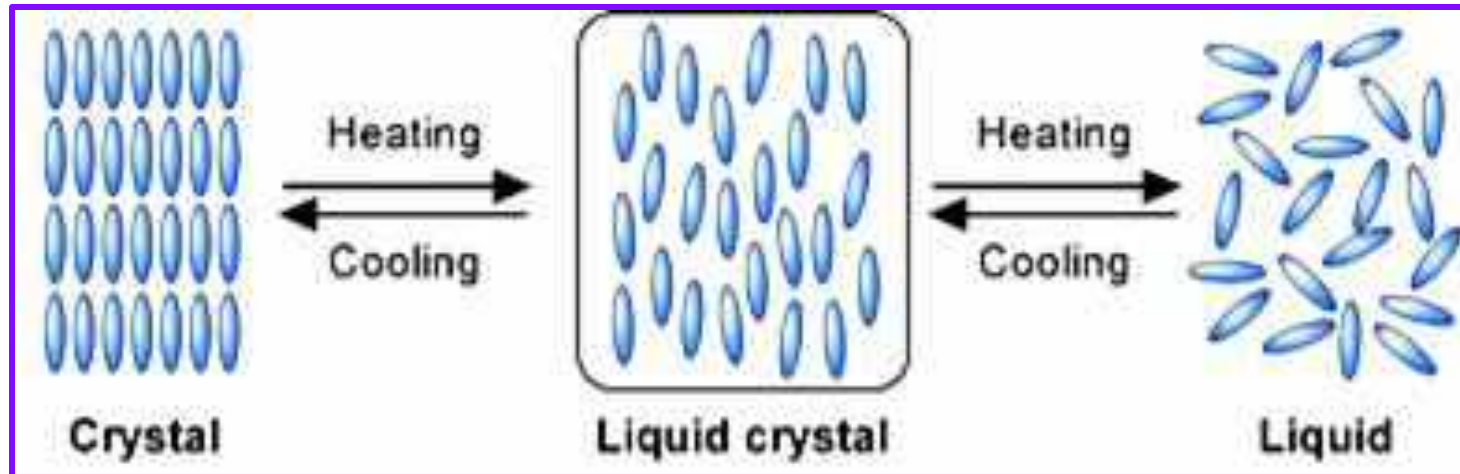
Classification of liquid crystals:



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.*





Thermotropic liquid crystals are further classified into:

- a) Calamatic L.C.(Rod like or elongated molecules)***
- b) Discotic Liquid Crystals (Disc shape molecules)***

Calamatic liquid crystals are elongated, rod shaped molecules. They are further classified as Nematic and Smectic liquid crystals.

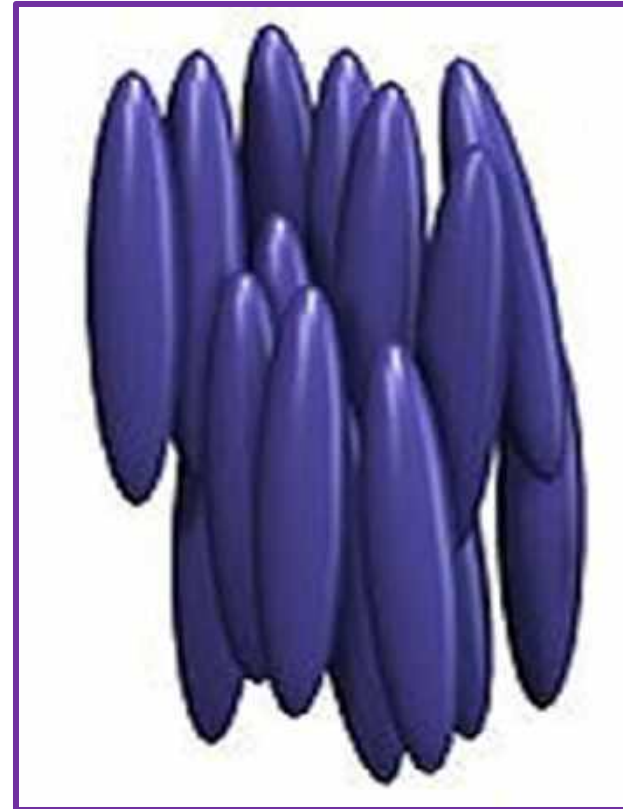


Nematic liquid crystals

- Word Nematic derived from Greek word *Nema* which means "thread".
- No positional order, but possess orientational 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 or 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).



Nematic liquid crystals can be further classified as:

a) **Ordinary nematic phases**: These molecules possess ordinary nematic phase characteristics as discussed earlier.

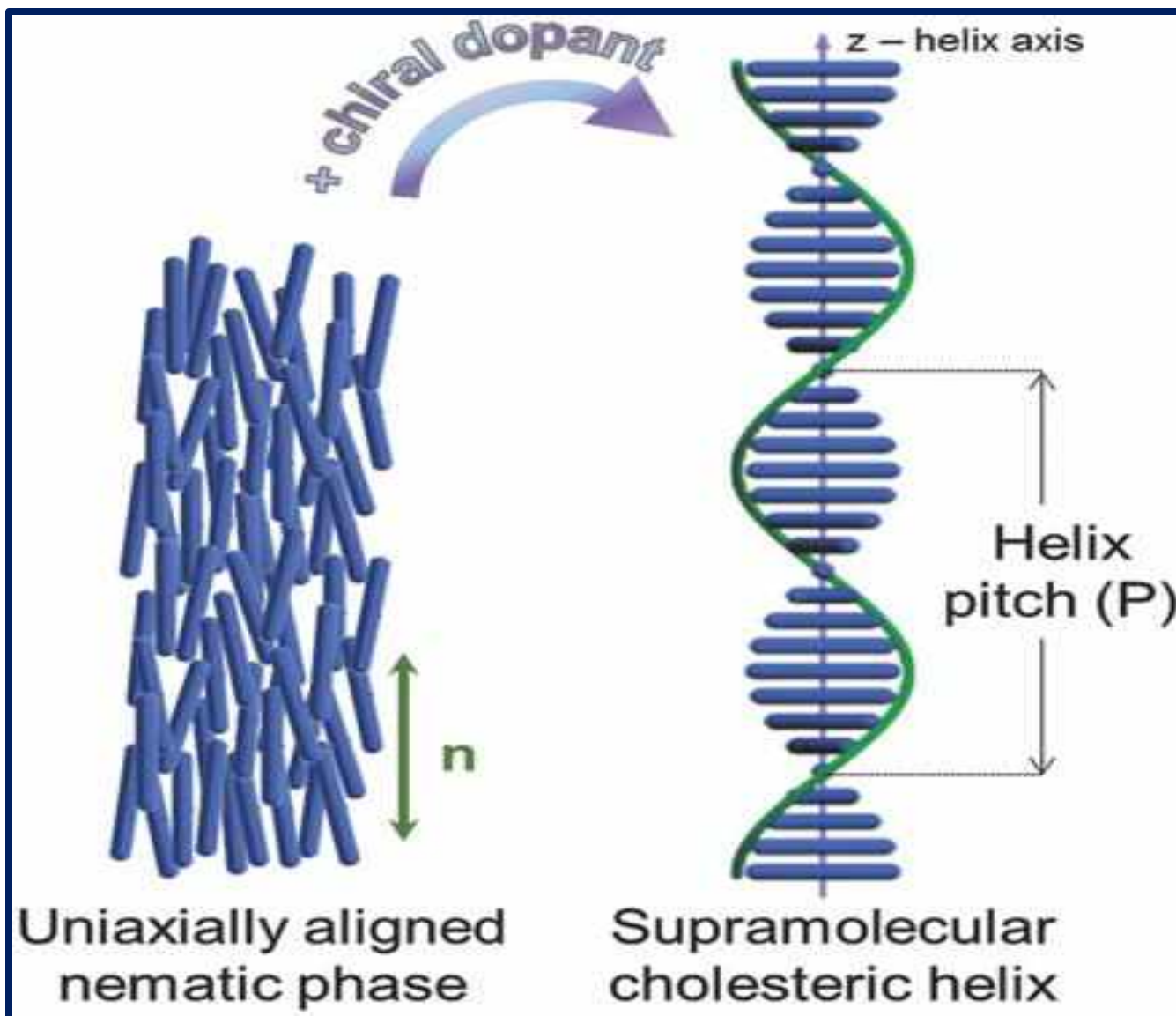
b) **Cholesteric nematic phases**: This phase is also known as chiral nematic phase. The molecules are essentially chiral and resembles nematic molecules in nature.



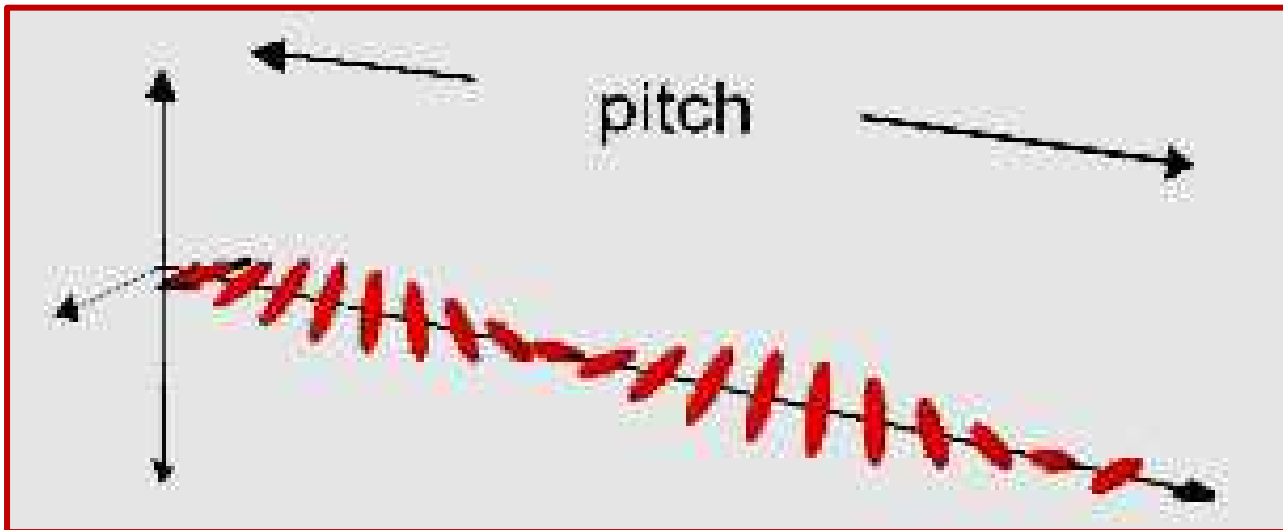
Cholesteric Liquid Crystals (Chiral Nematic)

- This phase is usually observed from cholesterol derivatives.
- The molecules are essentially chiral.
- The molecules are arranged in layers.
- These are formed by adding chiral twisting agent to the nematic liquid crystals.

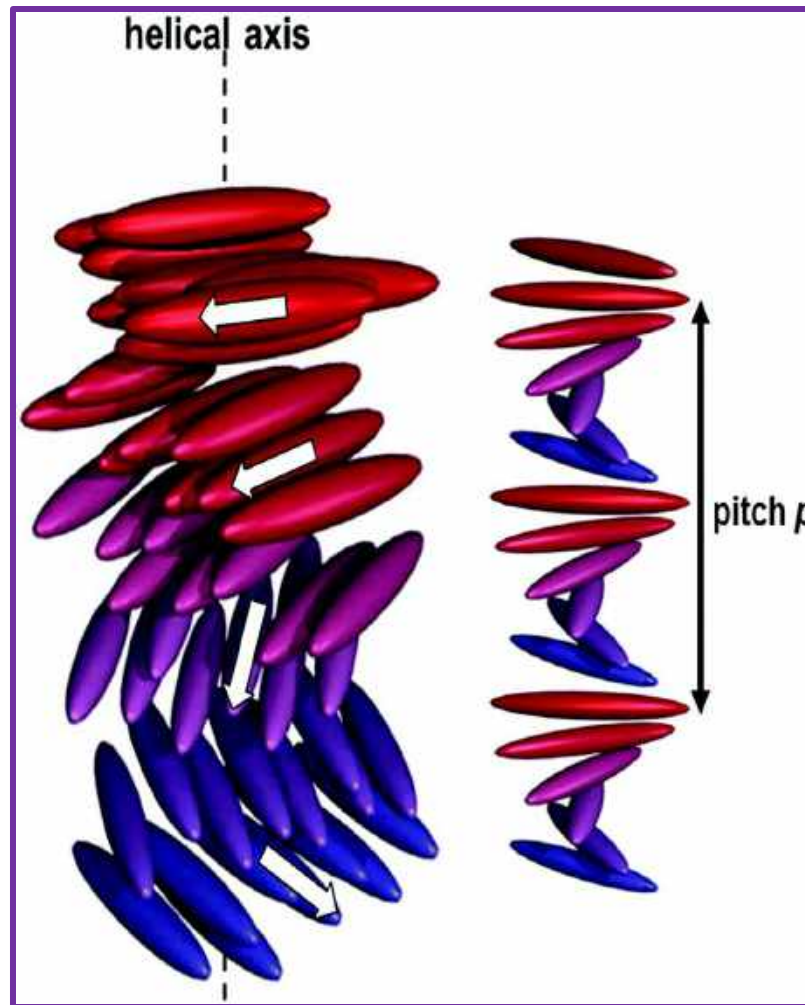




- Each layer in Cholesteric liquid crystal is tilted with respect to the other one, and hence the molecules take a one complete turn of 360 degrees to make a helix.
- The distance covered by the director in making a one complete turn is known as pitch.



- Cholesteric Liquid crystal reflects light approximately equal to pitch.
- Pitch is inversely proportional to the temperature.
- Pitch is affected by temperature, pressure as well as by electric and magnetic fields.



Smectic Liquid Crystals:

- Molecules are cigar shaped.
- Have short range orientational as well as positional order.
- 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.
- 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.
- Are of two types: Smectic A and C.
- E.g.: Ethyl-para-azoxyphenetole.

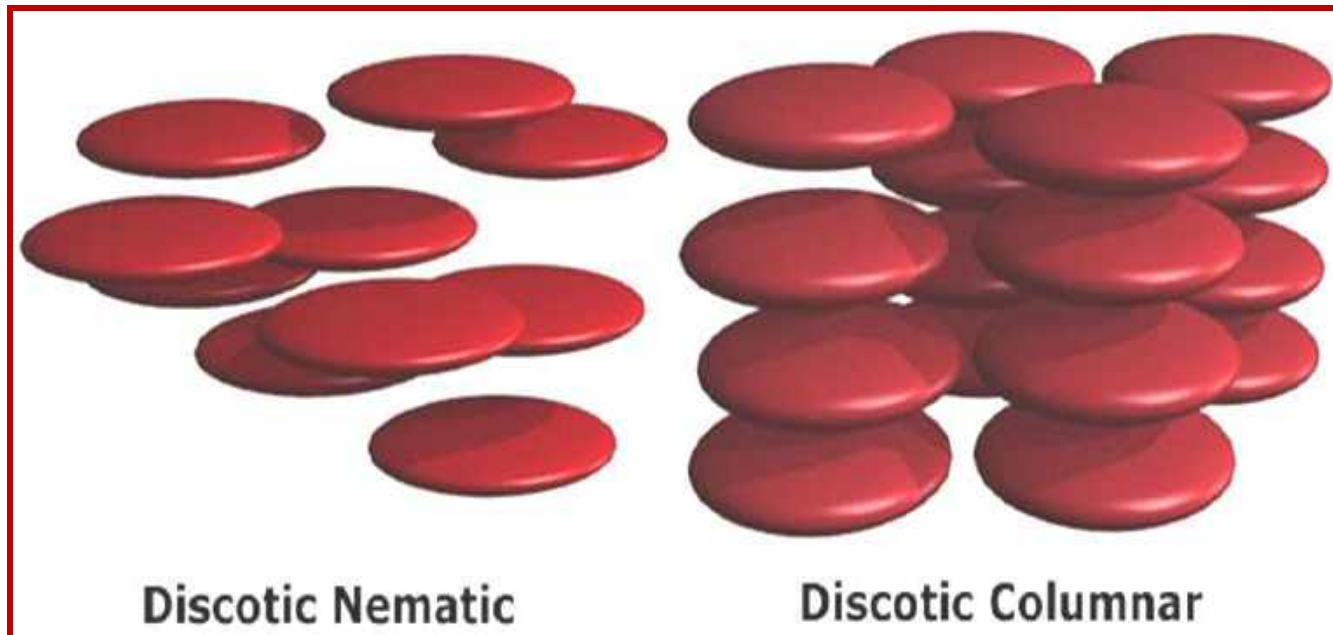


Discotic Liquid Crystals:

- 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 π conjugate systems. The charge transfer allows the discotic liquid crystals to be electrically semi conductive along the stacking direction.
- They are of two types: *Discotic nematic Phase and Columnar Phase*.



Disc-shaped molecules have a tendency to lie on top of one another forming either **discotic nematic phases** (with discs oriented similar to that of nematic phase i.e. not having position order but having orientation order) or **columnar phases** (have column-like structure).

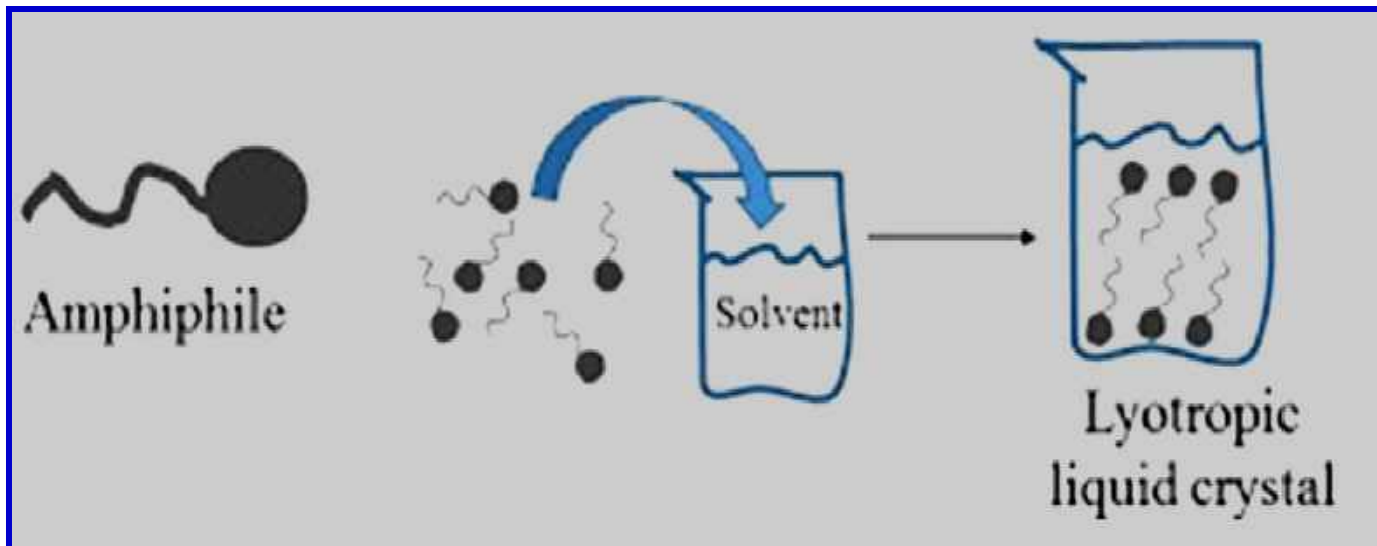


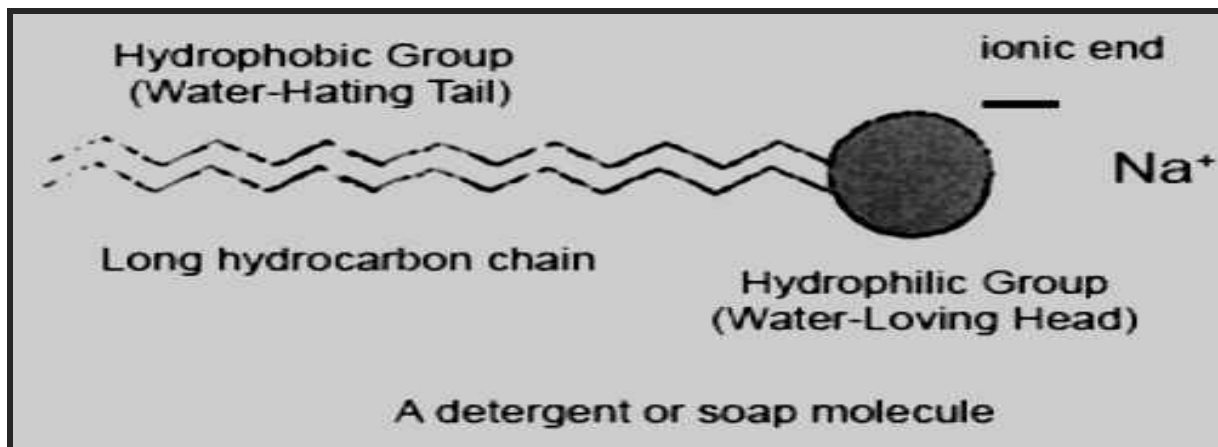
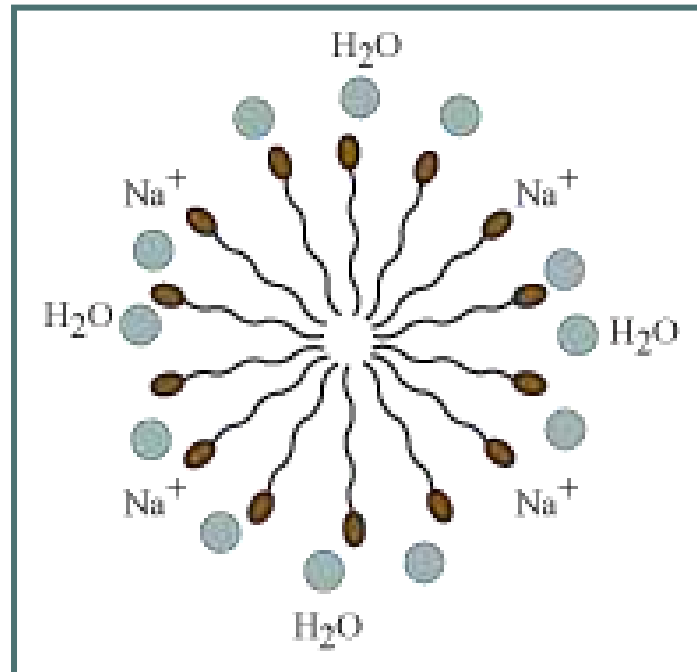
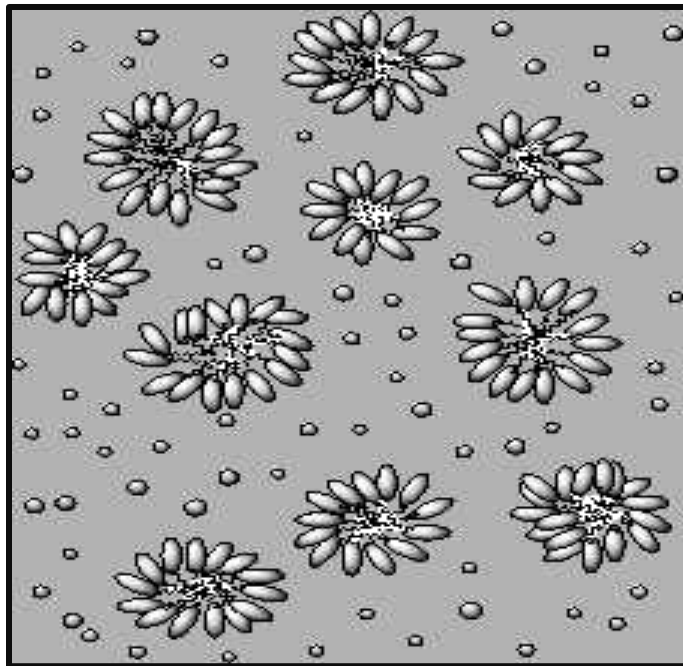
Lyotropic Liquid Crystals:

- Lyotropic liquid crystals are two component systems, where an amphiphile is dissolved in a solvent.
- Thus, lyotropic mesophases are solvent and concentration dependent.
- The amphiphilic compounds are characterized by two different moieties, a hydrophilic polar head and a hydrophobic tail.



- 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.
- **Examples:** molecules of soaps, phospholipids (present in cell membranes), toothpaste, many proteins and cell membranes, tobacco mosaic virus.





Three types of lyotropic liquid crystals are well known.

These are: **lamellar, hexagonal and cubic phases.**

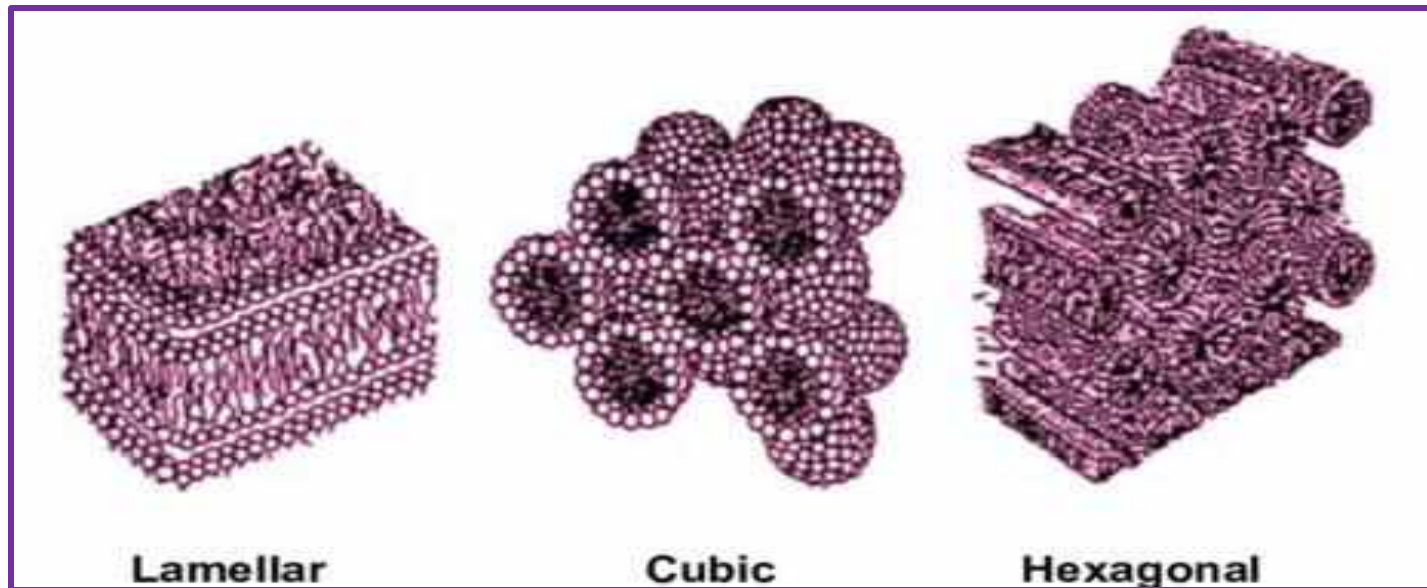
i) The simplest liquid crystalline phase that is formed by spherical micelles is the 'micellar cubic', denoted by the symbol **I₁**. This is a highly viscous, optically isotropic phase in which the micelles are arranged on a cubic lattice.

ii) At higher amphiphile concentrations the micelles fuse to form cylindrical aggregates of indefinite length, and these cylinders are arranged on a long-ranged hexagonal lattice.

This lyotropic liquid crystalline phase is known as the '**hexagonal phase**', and is generally denoted by the symbol **HI**.



iii) At higher concentrations of amphiphile the '**Lamellar Phase**' is formed. This phase is denoted by the symbol L_{α} . This phase consists of amphiphilic molecules are arranged in bilayer sheets separated by layers of water.




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.
- Have Medical applications like localized drug delivery.
- To detect radiations& pollutants in atmosphere.
- Used in non-destructive testing.
- Cholesteric liquid crystals are used in coloured thermometers.
- Used to locate tumours, veins, arteries, infections, foetal placenta etc.





Green Normal
35.0-37.1°C
(95.0-98.8F)

Yellow Elevated
37.2-37.9°C
(98.9-100.3F)

Red Fever
38.0-43.9°C
(100.4-111.0F)



Industrially important Liquid Crystal

Liquid Crystal have been intensively studied as functional materials. Industrially important materials based on liquid crystals are nonmaterial, polymer blends, reinforced materials, elastomers, flexible glass are follows.

1. Liquid Crystal polymer (LCP's)
2. Liquid Crystal Elestomers (LCE's)
3. Liquid Crystal Glass
4. Nonmaterial enhanced liquid crystalline Material
5. Liquid Crystal as reinforced material



1. Liquid Crystal polymer (LCP's)

- Liquid crystal polymers are polymers with the property of liquid crystal, usually containing aromatic rings as mesogen. They have excellent mechanical and electrical properties and outstanding chemical resistance.
- E.g. Ultra-high strength and light weight fibers and cables, bulletproof vest, tennis strings and hockey sticks. These includes Kevlar and vectra polymer.



2. Liquid Crystal Elastomers (LCE's)

- LCE films can be used as optical retarders due to their anisotropic structure because they can control the polymerization state of transmitted light . They are commonly used in 3D-glass, patterned retarders for transflective displays and flat panel LC display.
- LCEs are used to make actuators and artificial muscles for robotics.



- Azobenzene containing liquid crystal elastomers (AzBz-LCE) can be chosen as one of the optimal electronic liquid crystal elastomer for structuring organic electronic systems used for application in drugs and foods because they have properties of both liquid crystal and elastomers.



3. Liquid Crystal Glass

- Liquid Crystal glasses are most widely used in digital devices industry. These glasses provide the flexibility and reduced thickness in the displays.
- Eg. Amorphous silicon active matrix LCD (AM LCD)



4. Nonmaterial enhanced liquid crystalline Material

- Nonmaterial enhanced liquid crystalline properties such as threshold voltage, response time, viscosity, dielectric anisotropy, refractive index which are important in the area of LC displays (LCD's)



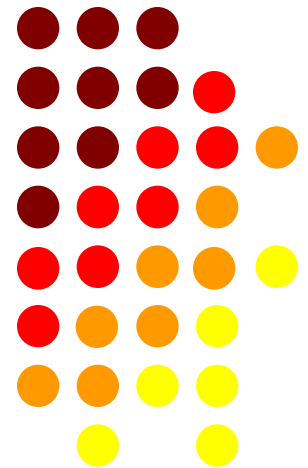
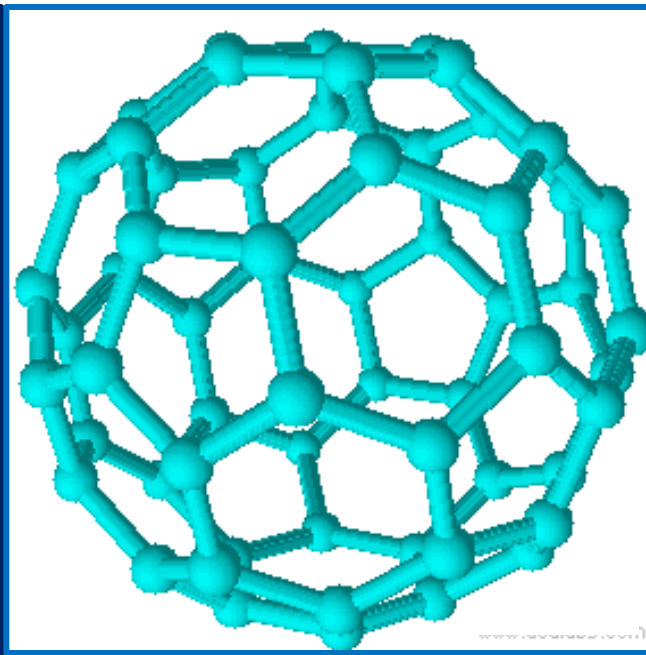
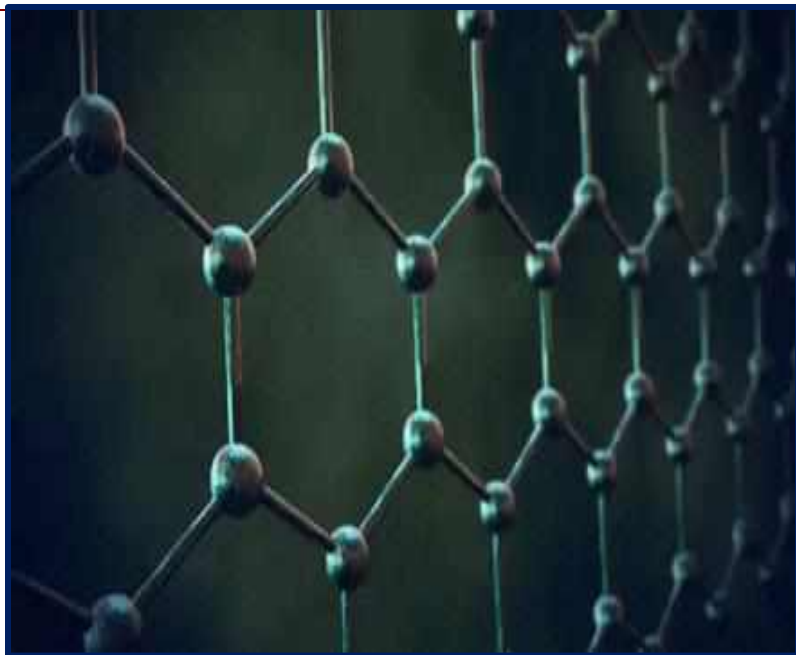
5. Liquid Crystal as reinforced material

- By the copolymerization of p-hydroxy benzoic acid and phthalic acid with ethylene glycol resulted in the reinforced material which provide the strength and stiffness to thermotropic polymer. These are also used as a reinforcing fillers in thermoplastic fillers.



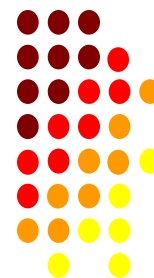
LECTURE - 5

Structure and Applications of Graphite and Fullerenes



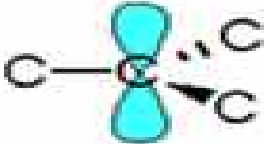
Graphite: An allotrope of Carbon Structure of graphite:

- Graphite is an allotrope of carbon (it is made up of only pure carbon atoms).
- Each carbon atom in graphite is *sp² 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 Å) with other carbon atoms.

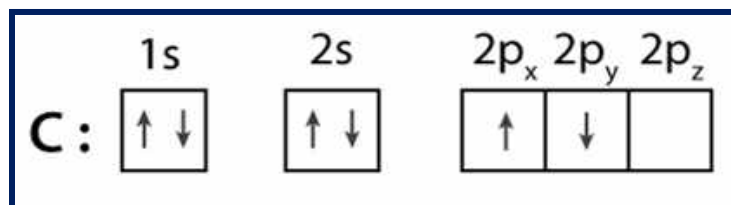


- Fourth electron of each carbon atom is free to move within the layer.
- Various hexagons join together to form a plane or sheet called ***graphene***.
- Various sheets (graphene) are arranged one above the other.
- Different layers of graphite are attached to each other with ***weak Vander Waals forces***.
- Distance between two successive sheets is ***3.41 Å***.
- Graphite has ***planar, two dimensional*** structure.

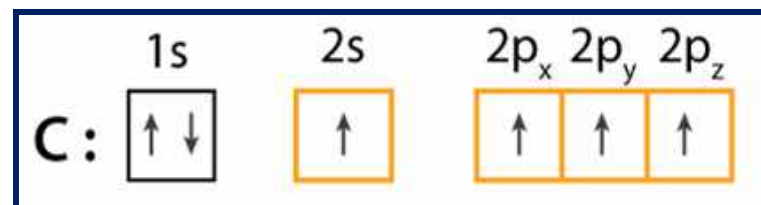


| | | |
|----------------------|-----------------|--|
| Name of the Molecule | Graphite |  <p>trigonal planar carbon in graphite with p orbital</p> |
| Molecular Formula | C | |
| Hybridization Type | sp^2 | |
| Bond Angle | 120° | |
| Geometry | Trigonal Planar | |

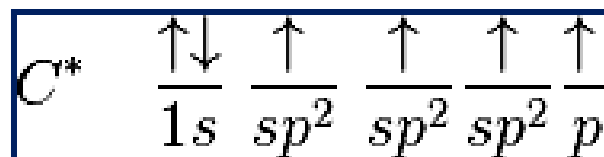
Hybridisation of C in graphite:



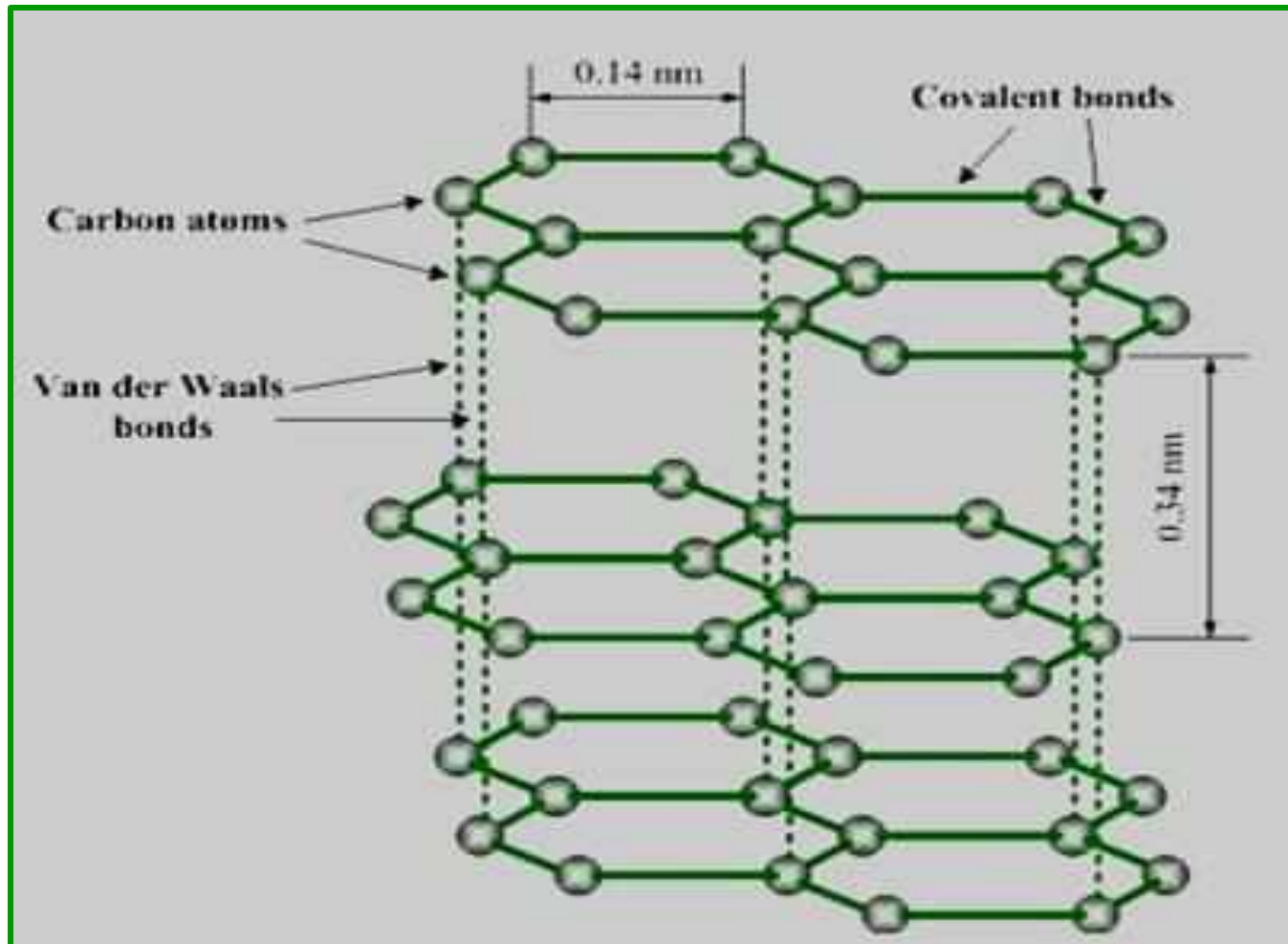
Ground state



Excited state



STRUCTURE OF GRAPHITE



Properties of Graphite:

- It is greyish ***black and greasy*** substance.
- Has ***metallic luster*** and is ***opaque to light***.
- ***High Melting point*** because the strong covalent bonds take long time to break.
- ***Slippery nature*** / Layers can slide one another due to weak Vander Waal forces of attraction between the two layers.
- ***Low coefficient of friction***.



- Ineffective in vacuum conditions.
- Thermodynamically more stable than diamond.
- Graphite exists in two forms: α -graphite and β -graphite.
- In spite of being non-metal, graphite is a ***good conductor of electricity*** due to the presence of free electron in p_z orbital of each carbon
- ***Density 1.25g/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.
- It is used in the ***preparation of electrodes*** as it conducts electricity due to presence of free electron on each carbon atom.



- Due to high melting point it is used ***to prepare crucible*** for making high grade steel.
- It is used as ***moderator in nuclear reactors*** as it absorbs fast moving neutrons.
- Used as ***conductive ink for screen printing***.



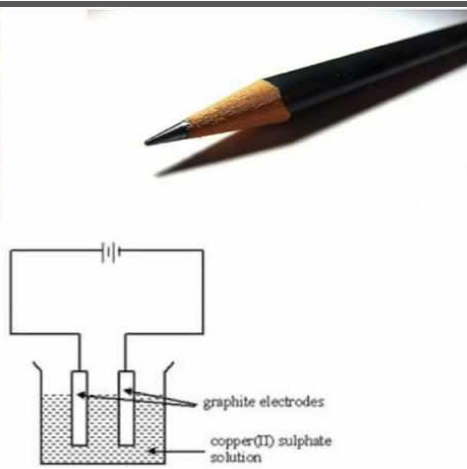
Crucibles made of graphite



Graphite conductive ink for screen printing



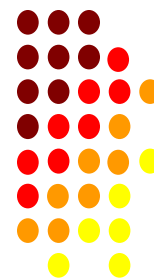
Uses of Graphite



Fullerene

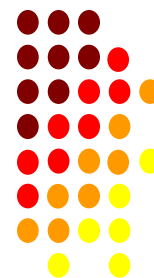
(Discovered by Kroto&Smalley)

- It is an allotrope of carbon, also called *buckminster fullerene* or *Bucky Ball*.
- Fullerenes exist as C_{60} , C_{70} , etc. The canonical structure, C_{60} , has *icosahedral symmetry* and an electronic structure similar to that of graphene.
- C_{60} is the most stable & widely used member of fullerene family.

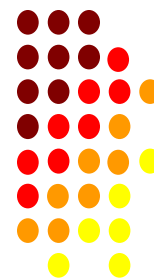
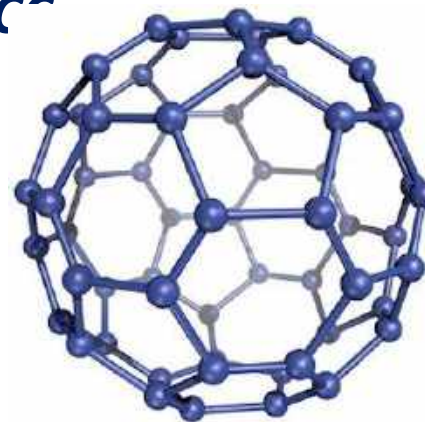
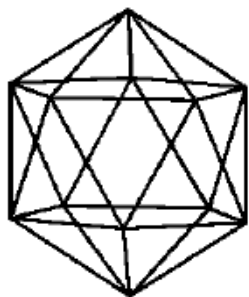


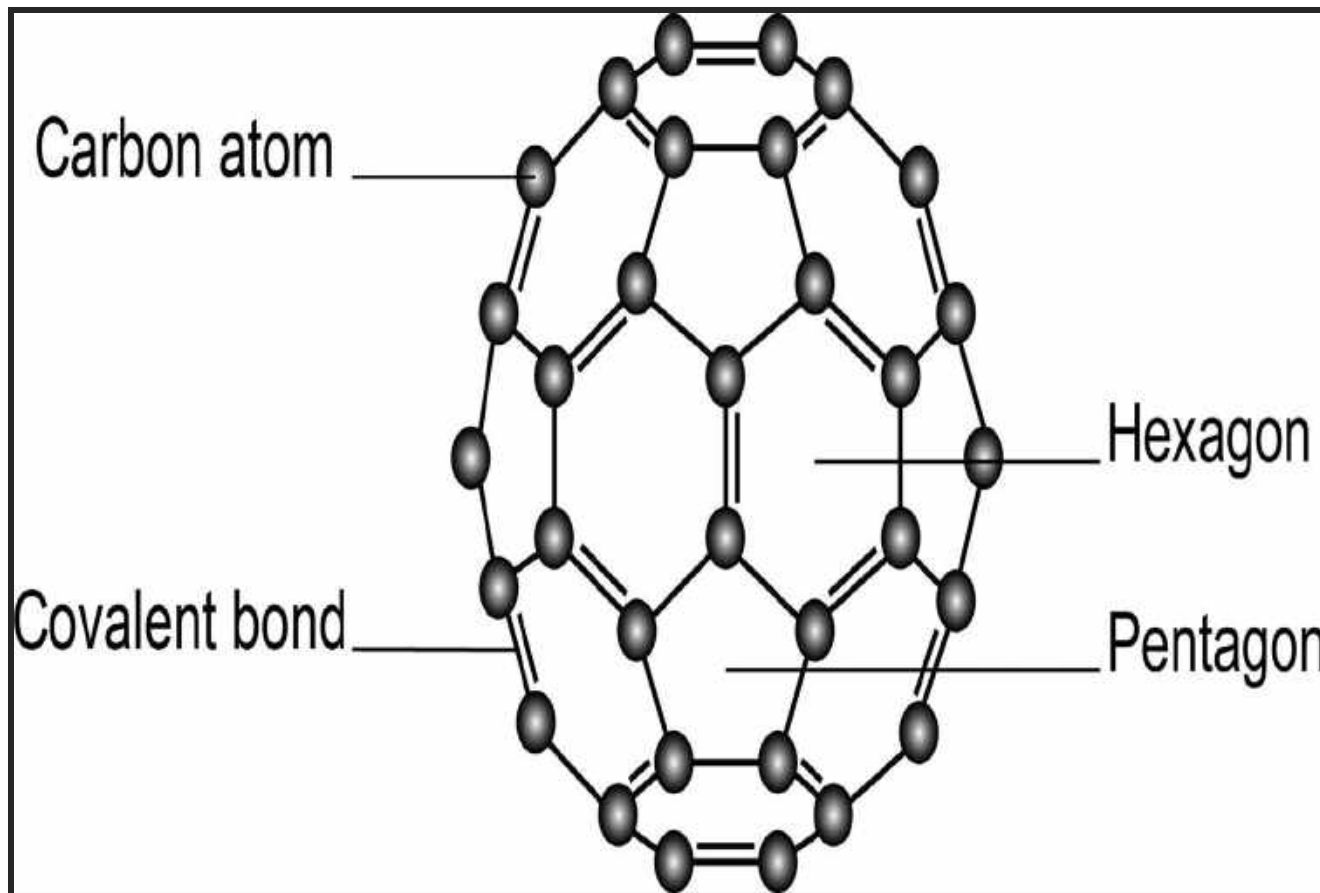
Structure of C₆₀

- Made up of **60 carbon** atoms.
- Each carbon atom is ***sp² 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 C₆₀ molecule is **7Å**; geometry- ***truncated icosahedron or geodesic dome***.
- There are **30 (C=C) double bonds** in C₆₀.

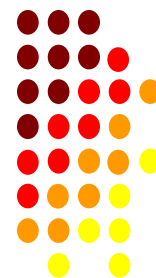


- There are **60 vertices, 32 faces**.
- C-C single bond length- 1.45\AA ; C=C double bond length= 1.38\AA
- It is highly symmetrical molecular & is said as **zero dimensional**.
- Has tendency to avoid double bonds in pentagon rings.
- Fullerene crystal structure is FC_{60}





Structure of fullerene



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.



Preparation of Fullerene:

Graphite rods kept in an inert atmosphere (He gas) at .05 to .1 atm pressure.

↓ *Electric current*

Rods evaporate to give fullerene soot (light and fluffy dust) Containing 5 to 15 % fullerenes.

↓ *Sublimation*

Fullerene mixture

↓ *Chromatography using alumina hexane*

C_{60}



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.

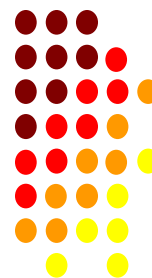


- Exists as discrete molecule unlike graphite or diamond.
- Pentagon of a fullerene are more strained than the hexagon, so at higher temp., fullerene molecule break at pentagon sites.
- It is possible to trap some ions inside fullerene cage or attach some functional molecules to fullerene from outside.
- Can be compressed to lose 30% of its original volume, without destroying the carbon edge structure.



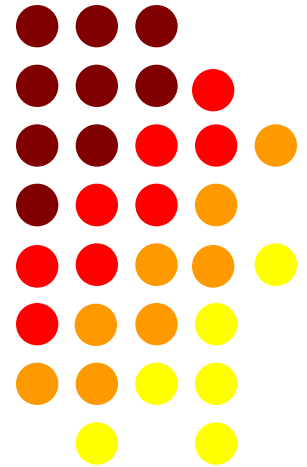
Uses of Fullerene

- Have powerful antioxidant properties, so used in health & personal care areas.
- C_{60} shows catalytic process.
- Act as drug delivery agent.
- C_{60} 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.



Carbon Nanotube

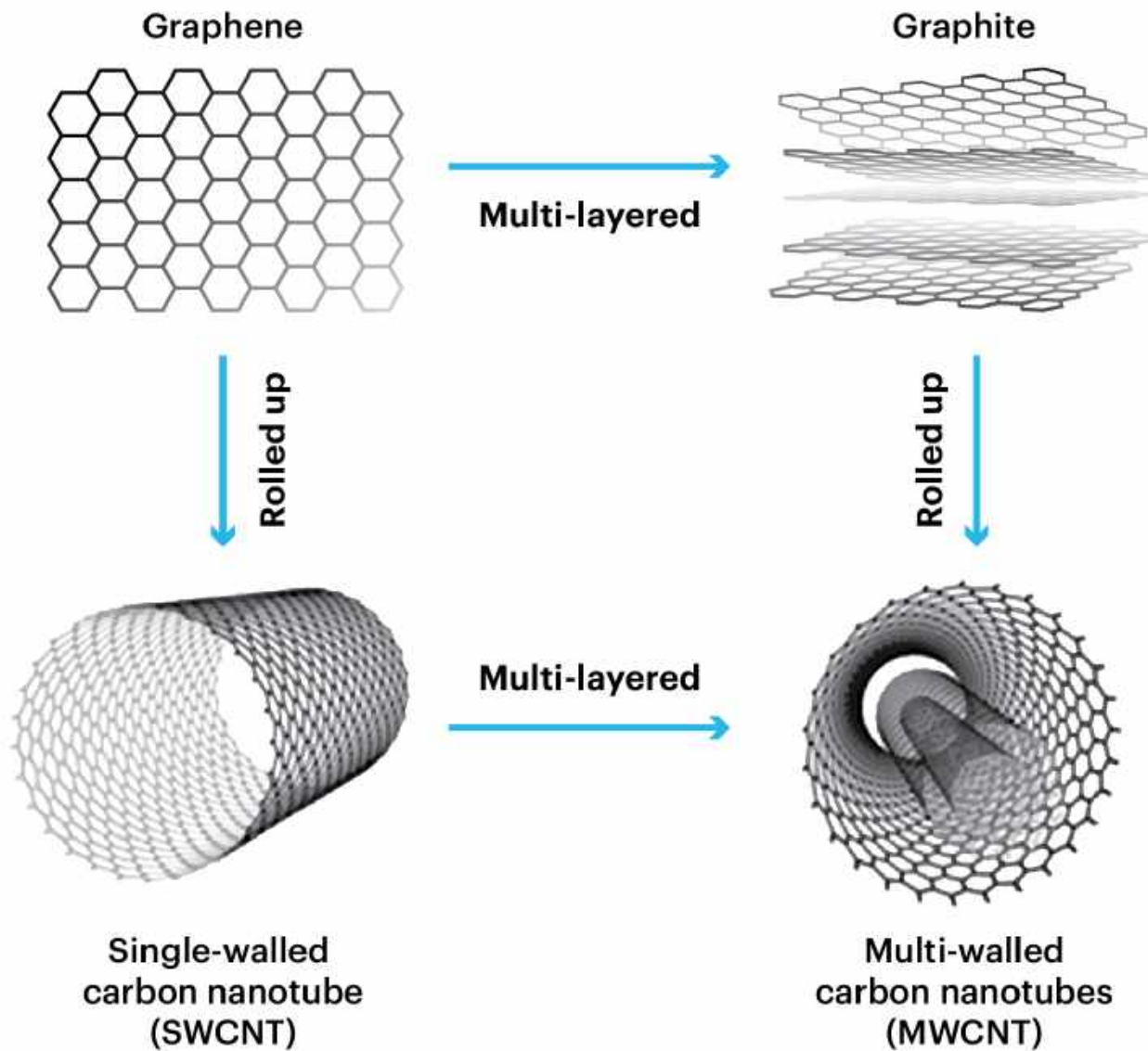
- **Introduction**
- **Silent feature**
- **Properties**
- **Types of CNT**



Introduction

CNT is one of the most important nanomaterial at present time. Before 1991, only 2 allotropes of carbon were known namely Diamond and Graphite. But in 1991, Japanese physicist Sumio Iijima discovered another allotrope of carbon called carbon nanotube. When we roll up 2D graphite (*Graphene*) sheet into a cylindrical tube, we get CNT. The diameter of CNT is about 1-3 nm and can have length upto few micrometer. CNT exhibit extraordinary mechanical properties



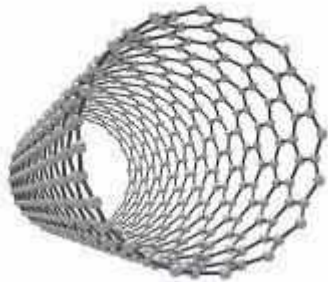


Silent feature of CNT

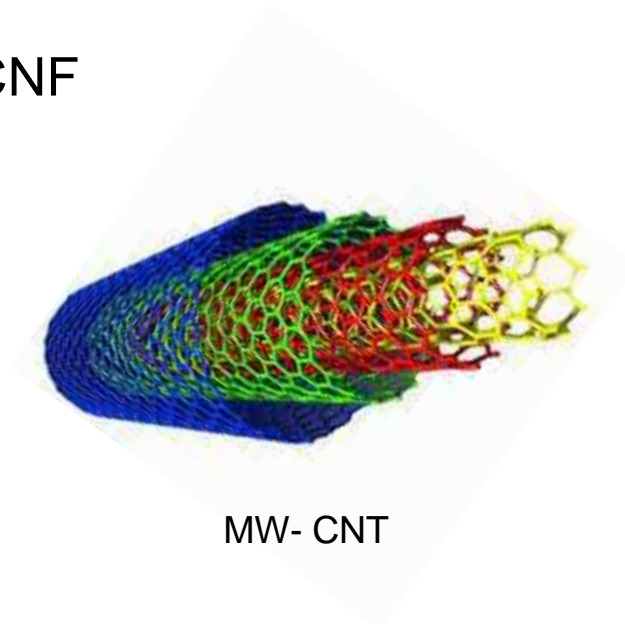
- They are stiff as diamond.
- They are light weight.
- Their density is $1/4^{\text{th}}$ of that of steel and thermal opacity is 20 times more than steel.
- In CNT each carbon atom is bounded to 3 other carbon atoms through covalent bonds and forms a lattice in the shape of hexagons
- Outer diameter : 2-20 nm
- Inner diameter: 1-3 nm
- Length: 1-6 μm



- MWCNT are different from carbon nanofibre (CNF). CNF have diameter of 200 nm and they are not hollow from inside.
- CNF have been in use for several decades to strengthen compound but their lattice is different from CNT.
- CNT is improved version of CNF



SW- CNT



MW- CNT



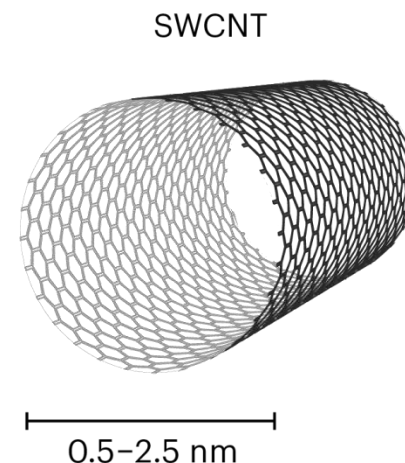
Properties of Carbon nanotubes

- CNT as elastic-tensile strength of CNT is about 200 Giga Pascal and therefore CNT can be stretched 20% of their rest length and can be bent and even tied a knot with no resulting effect.
- CNT are good conductor of heat- they have very high thermal capacity. So thermal expansion produced in CNT is very small
- CNT have good electrical conductivity – CNTs have very few defect so they can carry billion ampere of current /cm
- CNT are very strong- CNTs are 10 times stronger than steel.
- Chemically stable- They are resistant to corrosion.



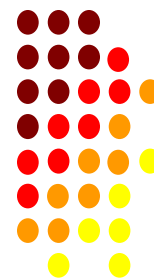
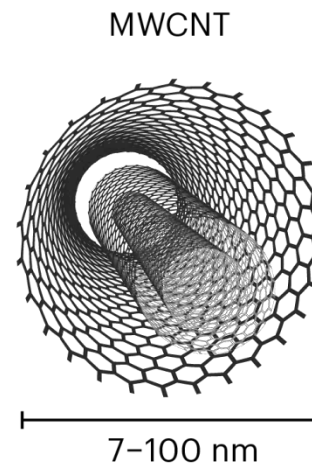
Type of Carbon nanotube

- Single Walled Carbon Nanotube (SW-CNTs)
- Diameter 0.5-2.5 nm , length 2 μm
- Aspect ratio is typically greater and often goes up to 10,000
- It posses 1-D structure and is called Nanowire. Eg. Armchair and Zig Zag SWCNT
- SWCNT is used in electronics
- Their band gap is from 0 to 2 eV and they can exhibit both metallic and semiconducting behavior.



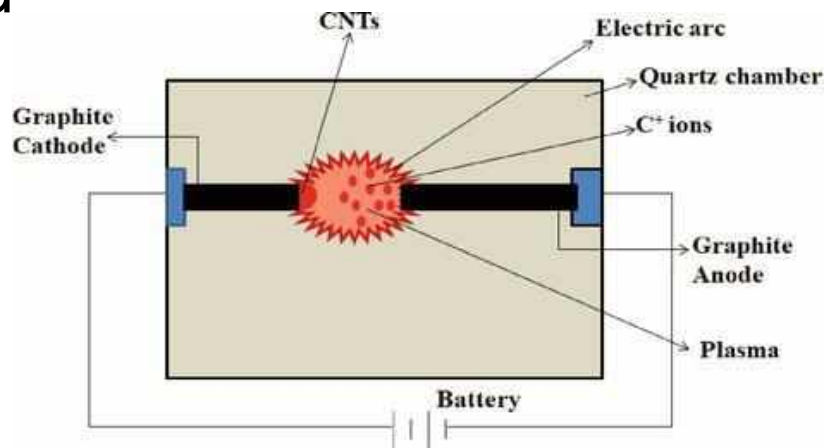
Type of Carbon nanotube

- Multi Walled Carbon Nanotube (SW-CNTs): It consist of several nested coaxial single walled CNTs. E.g. Chiral MW-CNT
- Aspect ratio is typically between 50 and 4,000



Preparation Method of CNTs

1. synthesis of CNTs by Electric arc discharge method



In this method, a potential of 20–25 V is applied across the pure graphite electrodes separated by 1 mm distance and maintained at 500 torr pressure of flowing helium gas filled inside the quartz chamber



2. Carbon Nano Tubes (CNTs) are prepared by the catalytic decomposition of Methane (CH_4) at 680 degree Celcius for 120 minute, by using Nickel Oxide- Silica binary aerogels as the catalyst.



Application of CNTs

1. Composite material containing CNT are being used in sports accessories like bicycle frames, tennis rackets, hockey sticks etc.
2. CNTs are used to make Bullet Proof Jackets
3. CNTs can **reduced the** weight of aircraft and spacecraft upto 30%.



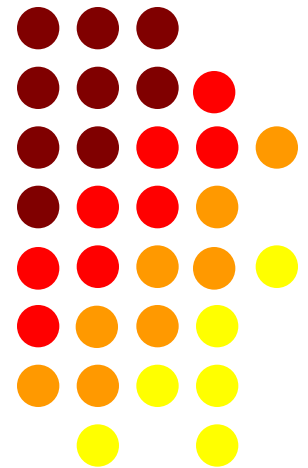
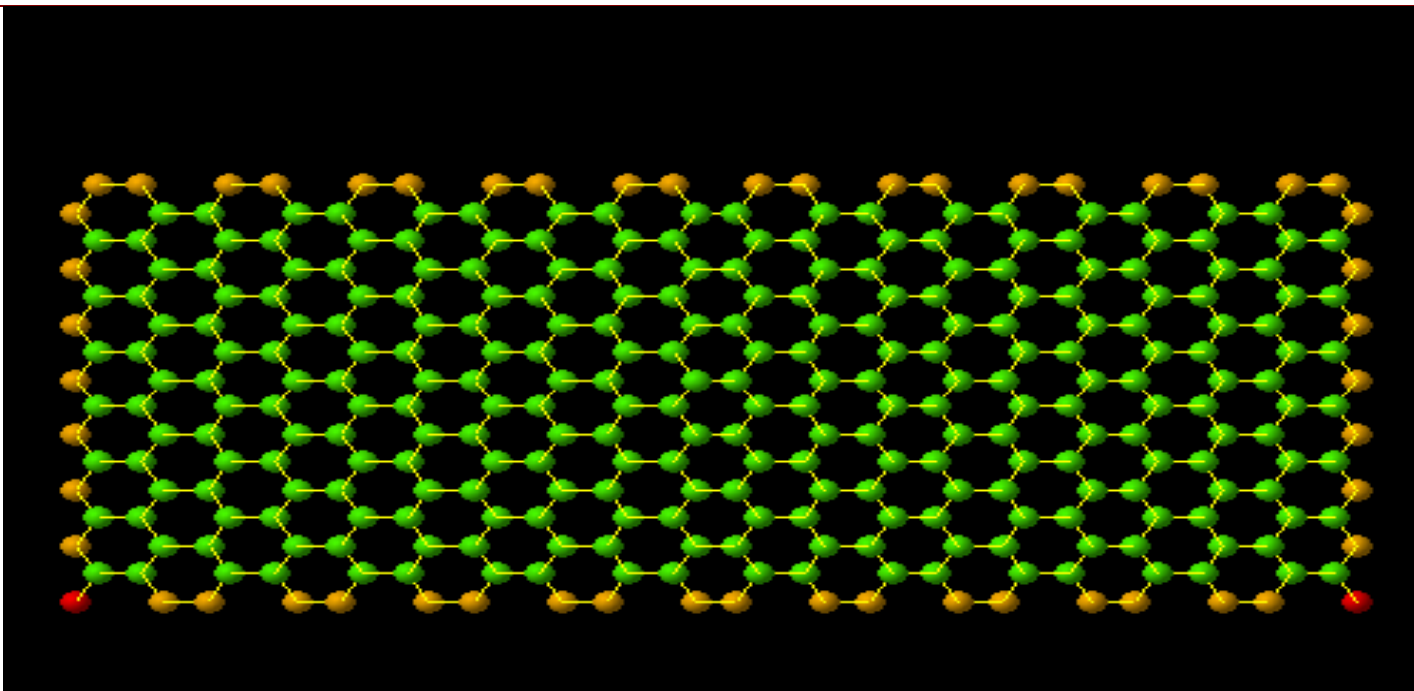
APPLICATIONS OF CNTs

4. CNTs can be used to build high performance transistors to replace silicon based transistors because of semi-conducting properties of SWCNT.
5. CNTs can be used to manufacture biosensors and electrochemical sensors which are used to sense green house gases (CO₂, CH₄) in environment.
6. CNTs can be used to make electrodes.



LECTURE - 7

Concepts, Properties and Applications of Nano- Sciences and Nano- materials



Nanomaterials

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

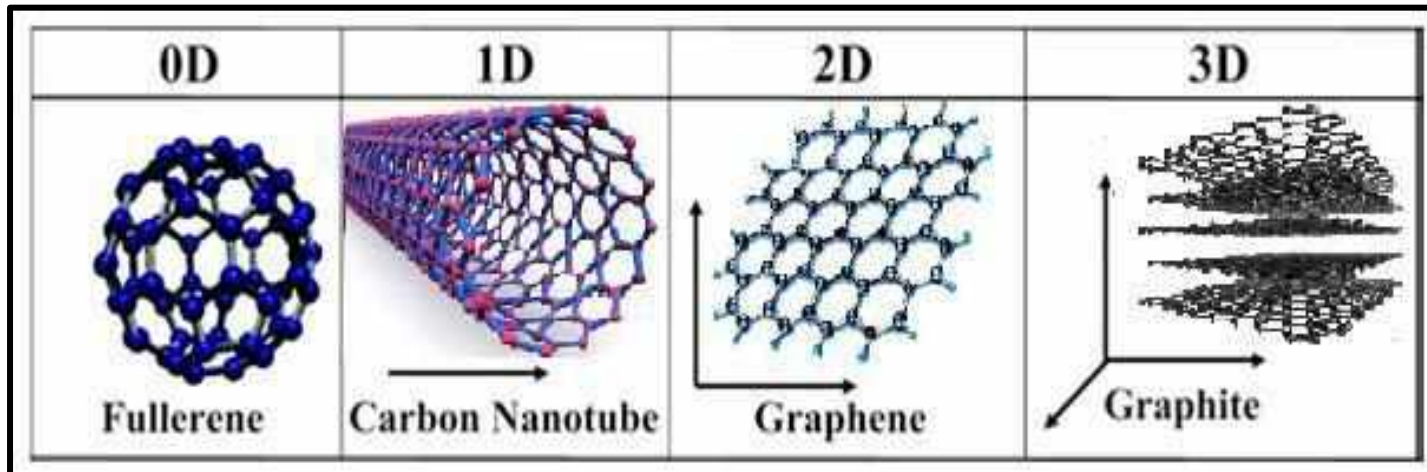
Nanotechnology: is the technology of manipulating a material and its properties at the nanoscale (atomic or molecular scale) for target-specific applications.

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



Various nano materials:

- Nano-particles
- Nano-wires
- Nano-tubes
- Nano-rods
- Nano-porous 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

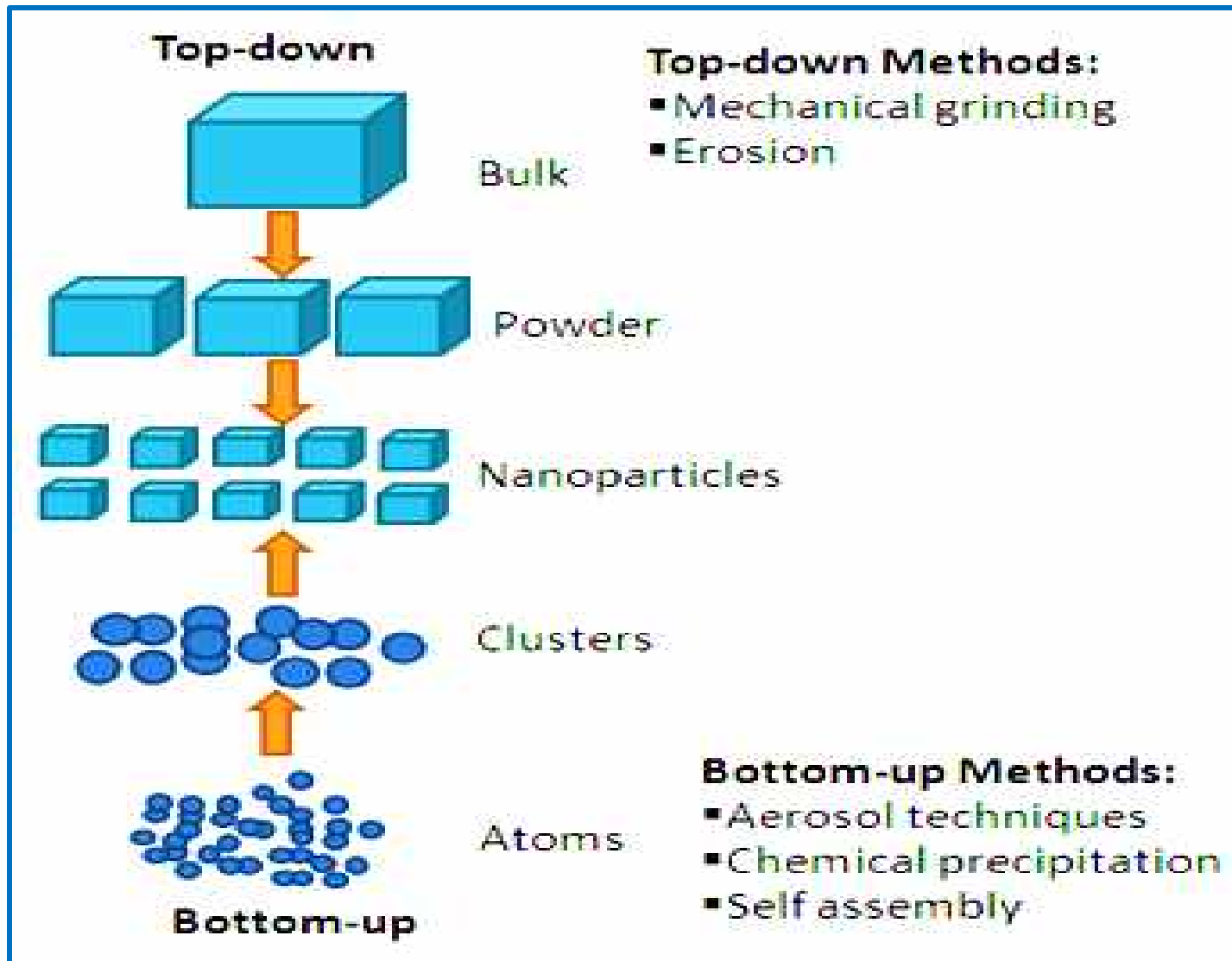


Nanomaterials synthesis approach:

1. **Top down approach:** The synthesis of nano particles using this approach includes built up of the structure by accumulation of each atom or molecule by molecule
2. **Bottom up approach:** This approach includes synthesis of nano particles by breaking down of bulk materials gradually into smaller sizes

Buildup of material: **Atom** → **molecule** → **cluster**

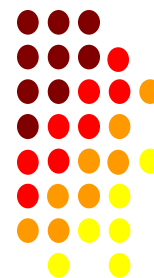




Applications of nanomaterials:

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

- Electronics
- Medicine
- Engineering and technology
- Industries
- Environment
- Sensors
- Catalysis

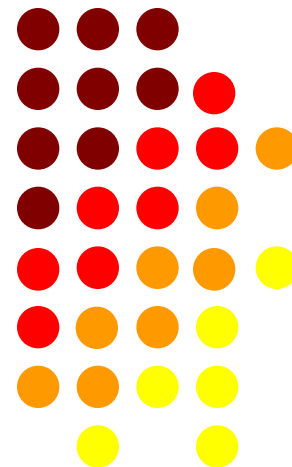


- Nano transistors, Field effect transistors.
- Field emission.
- Nano electrodes.
- Nano medicine, drug delivery systems, disease diagnosis.
- Chemical , bio, pressure, thermal sensors
- Nano devices.



LECTURE - 8

Introduction, 12 principles and importance of green Synthesis, Green Chemicals, Synthesis of typical organic compounds by conventional and Green route (Adipic acid and Paracetamol), Environmental impact of Green chemistry on society



Green chemistry

- Green chemistry referred to as sustainable chemistry is the branch of chemistry that deals with the design and optimization of processes and products in order to lower, or remove altogether, the production and use of toxic substances. Green chemistry is not the same as environmental chemistry.

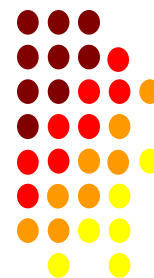


12 Principles of Green Chemistry

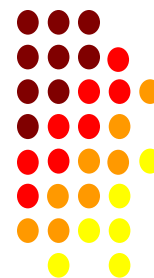
- **Prevention of waste:** Preventing the formation of waste products is always preferable to the clean-up of the waste once it is generated.
- **Atom economy:** The synthetic processes and methods that are devices through green chemistry must always try to maximise the consumption and incorporation of all the raw materials into the final product. This must strictly be followed in order to minimise the waste generated by any process.
- **Avoiding the generation of hazardous chemicals:** Reactions and processes that involve the synthesis of certain toxic substances that pose hazards to human health must be optimised in order to prevent the generation of such substances.
- **The design of safe chemicals:** During the design of chemical products that accomplish a specific function, care must be taken to make the chemical as non-toxic to humans and the environment as possible.



- **Design of safe auxiliaries and solvents:** The use of auxiliaries in processes must be avoided to the largest possible extent. Even in the circumstances where they absolutely need to be employed, they must be optimized to be as non-hazardous as possible.
- **Energy efficiency:** The amount of energy consumed by the process must be minimized to the maximum possible extent.
- **Incorporation of renewable feedstock:** The use of renewable feedstock and renewable raw materials must be preferred over the use of non-renewable ones.
- **Reduction in the generation of derivatives:** The unnecessary use of derivatives must be minimized since they tend to require the use of additional reagents and chemicals, resulting in the generation of excess waste.



- **Incorporation of Catalysis:** In order to reduce the energy requirements of the chemical reactions in the process, the use of chemical catalysts and catalytic reagents must be advocated.
- **Designing the chemicals for degradation:** When designing a chemical product in order to serve a specific function, care must be taken during the design process to make sure that the chemical is not an environmental pollutant. This can be done by making sure that the chemical breaks down into non-toxic substances.
- **Incorporating real-time analysis:** Processes and analytical methodologies must be developed to the point that they can offer real-time data for their monitoring. This can enable the involved parties to stop or control the process before toxic/dangerous substances are formed.



- **Incorporation of safe chemistry for the prevention of accidents:** While designing chemical processes, it is important to make sure that the substances that are used in the processes are safe to use. This can help prevent certain workplace accidents, such as explosions and fires. Furthermore, this can help develop a safer environment for the process to take place in.

EXAMPLES

- Green solvents
- Synthetic techniques
- Carbon dioxide as processing agent
- Carpet tile backings
- Transesterification of fats



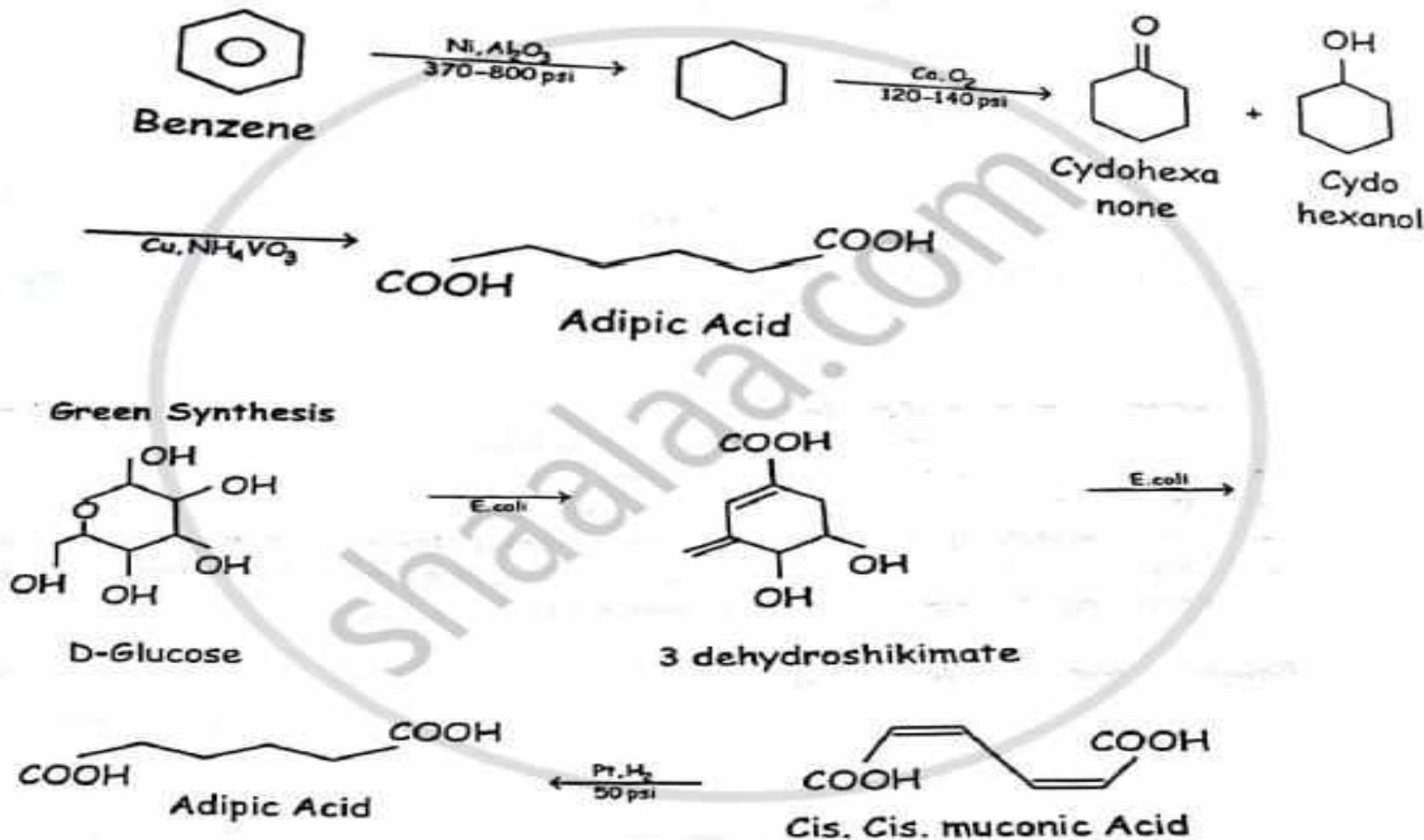
Green Chemicals



Green chemical is one that provides higher performance and functionality while being more environmentally benign throughout its entire life-cycle. This approach has been codified in the **Twelve Principles of Green Chemistry** that provide a framework for innovation and design.



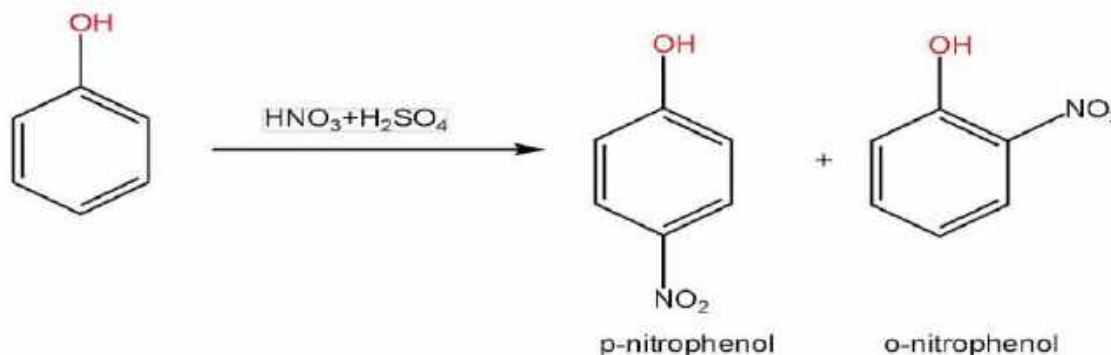
Synthesis of adipic acid by conventional and Green route



Synthesis of Paracetamol by conventional route

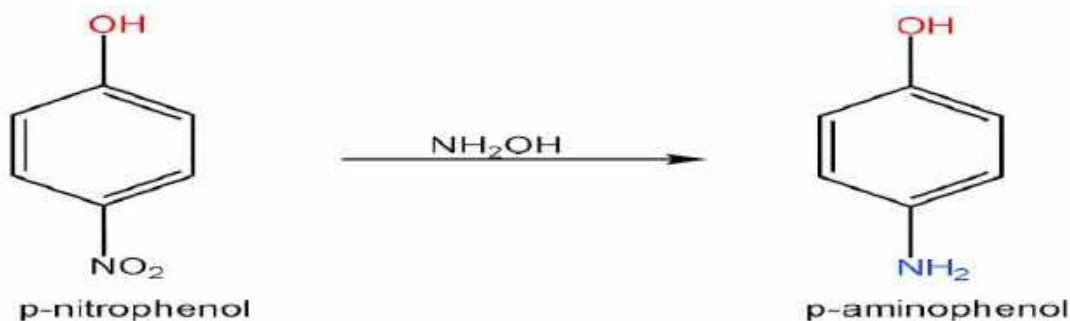
Step-1

When nitric acid is added to phenol, phenol undergoes nitration to form Nitrophenol and p-Nitrophenol, p-Nitrophenol is a major product.



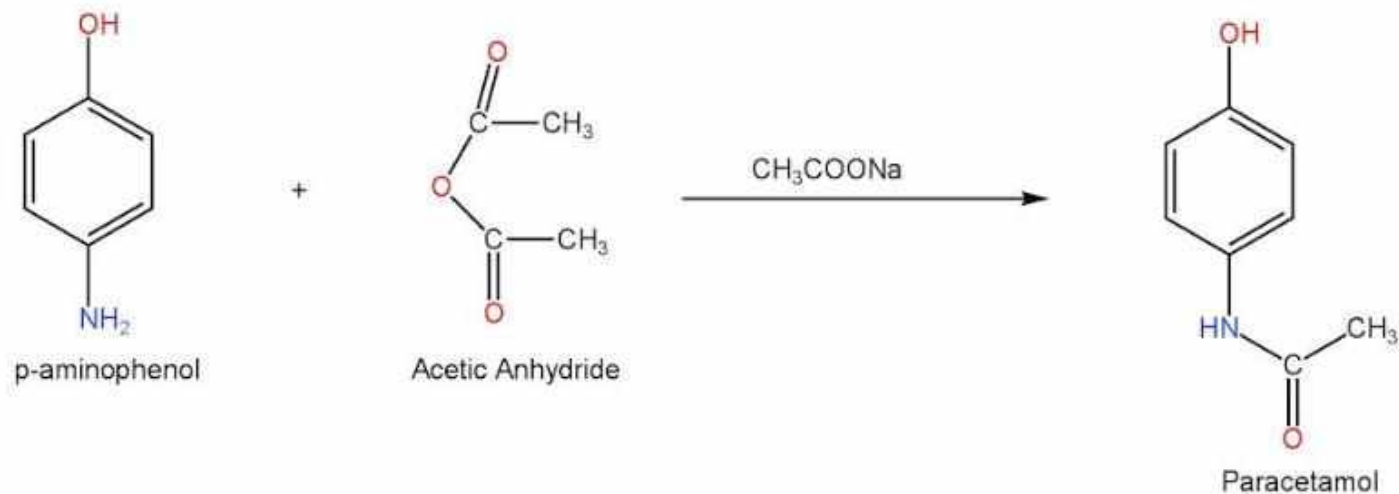
Step -2

Reduction of Nitro group (-NO₂) to amine group (-NH₂) group



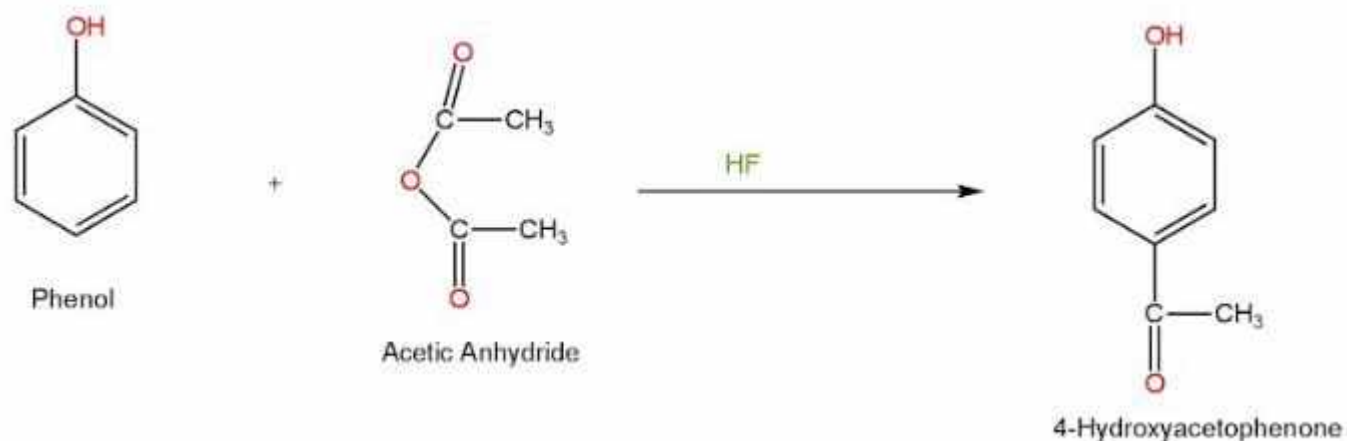
Step 3

- Nucleophilic addition reaction of p-aminophenol with acetic anhydride ($\text{CH}_3\text{CO-O-OCH}_3$) in the presence of sodium acetate (CH_3COONa)

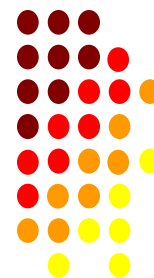
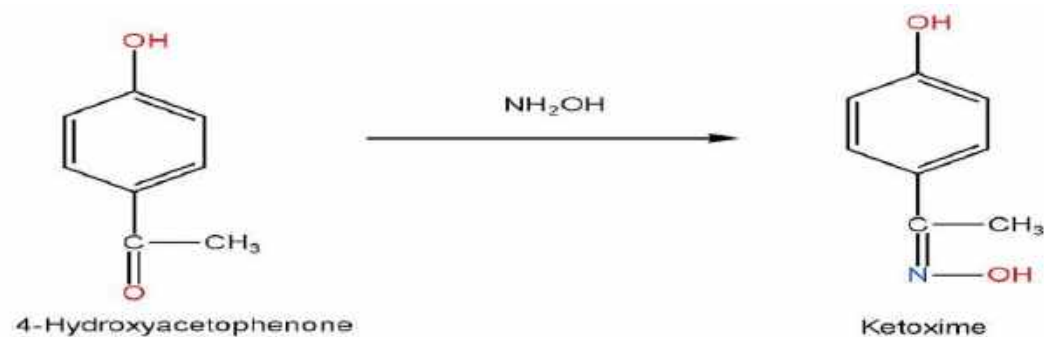


Green Synthesis of Paracetamol from Phenol

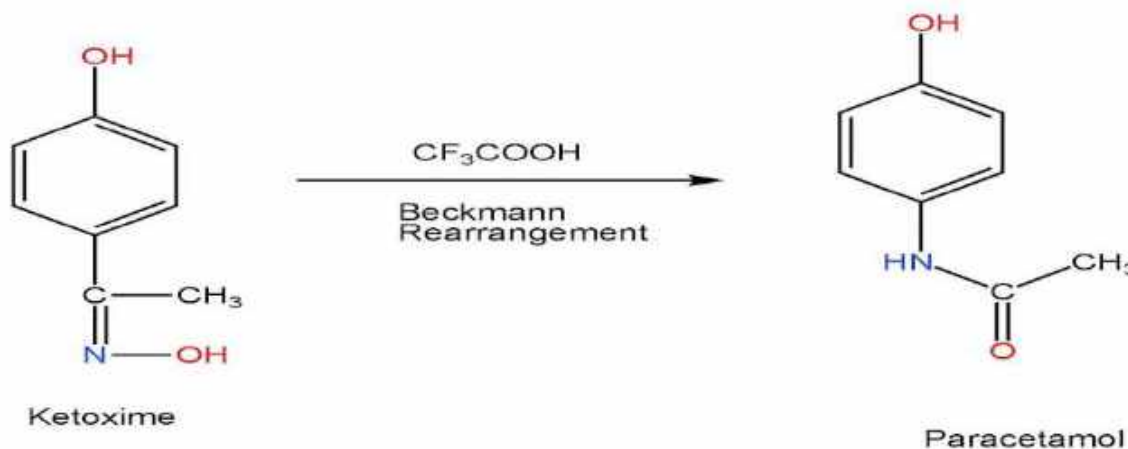
Step 1: Phenol reacts with acetic anhydride in the presence of strong acid like HF to undergo acylation reaction to give 4-hydroxyacetophenone.



Step 2 :Reaction of aldehydes and ketones with hydroxylamine (NH₂OH) gives oximes. 4- hydroxyacetophenone reacts with hydroxylamine to give corresponding ketoxime.

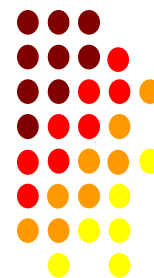


Step 3: Oximes in acidic medium (trifluoroacetic acid, CF_3COOH) undergoes Beckmann rearrangement to produce substitute amides. Beckmann rearrangement of the above ketoxime gives paracetamol.



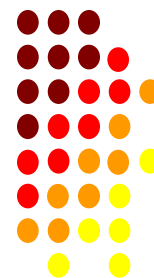
Uses of Paracetamol

- ✓ It is used as antipyretic drug to reduce body temperature in case of high fever.
- ✓ It is also used as a weak analgesic to reduce the mild to moderate pain (examples: head ache, tooth pain, menstrual pain, etc.)



Advantages of Green Chemistry :

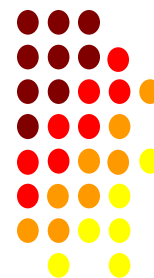
- Plants and animals suffers less harm from toxic chemicals in the environment.
- Lower potential for Global Warming.
- Ozone depletion and smog formation.
- Less chemical disruption of ecosystem.
- Less use of landfills, especially hazardous waste landfills.



Environmental impact of Green Chemistry on Society:

Through the practice of green chemistry, we can create alternatives to hazardous substances. The environmental impact of green chemistry on society can be listed as-

- Green chemistry is a proactive approach to pollution prevention
- Plants and animals suffer less harm from toxic chemicals in the environment.
- Lower potential for global warming, ozone depletion, and smog formation
- Less chemical disruption of ecosystems
- Less use of landfills, especially hazardous waste landfills.
- Cleaner air - Less release of hazardous chemicals to air leading to less damage to lungs
- Cleaner water - less release of hazardous chemical wastes to water leading to cleaner drinking and recreational water
- Less exposure to toxic chemicals



The four R of Green Chemistry

Refuse –

Learn to say no. Say no to single use plastic, say no to straws. Say no to items that will immediately go to landfill, and stay there - permanently.

Reduce –

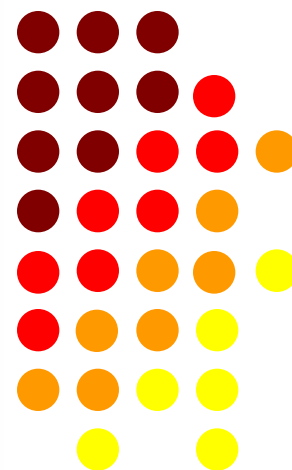
Don't impulse buy, and reduce your general consumption. Don't buy a million types of product and never use them. Simplify your life too and use multiuse and natural, homemade products. Reduce the amount of general waste you create.

Reuse –

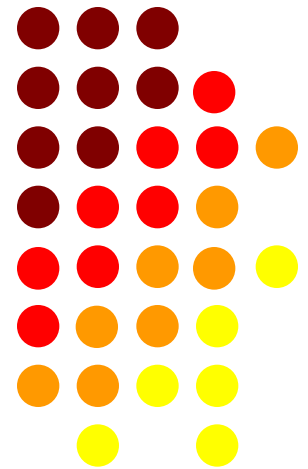
Stop using disposable products at all. Replace them with more sustainable alternatives. Say no to disposables and yes to reusables! If things break, try to fix & repair them instead.

Recycle –

After refusing, reducing and reusing, there shouldn't be much left to recycle. Just make sure you clean & separate your recycling properly, and recycle them in the correct place.



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THANK YOU

A watercolor illustration featuring the words "THANK YOU" in a black, serif font. The text is surrounded by various autumn-themed elements: several leaves in shades of red, pink, and orange, some with white vein patterns; small clusters of green berries; and a few small black starburst symbols. The overall style is soft and artistic.