

Unit - 1

Engineering Chemistry [KAS-102/202]

Lecture No.-1

(Introduction)

- Self Introduction
- Student's Introduction
- Introduction of Basics of chemistry-

Atom - Atom is the smallest constituent unit of matter.

Molecule - When two or more atom combine, the constituent unit is known as molecule.

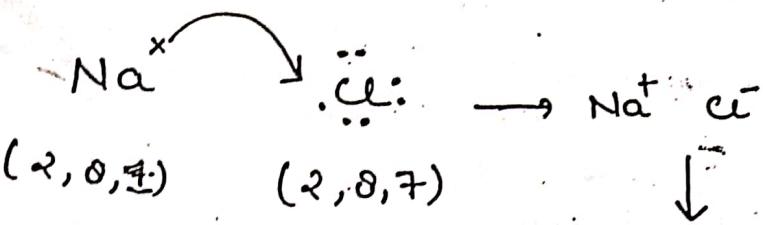
chemical-Bonding - "The force of attraction that binds the atom within a molecule is called chemical bonding." Bonding may be of following types-

- (A) Ionic Bond
- (B) Covalent Bond
- (C) Metallic Bond

(A) Ionic Bond - "A bond formed by complete transference of one or more electrons from highly electropositive element to highly electronegative element is known as Ionic Bond."

Ex: $_{11}^{Na} - 1s^2 2s^2 2p^6 3s^1$ (Electropositive)

$_{17}^{Cl} - 1s^2 2s^2 2p^6 3s^2 3p^5$ (Electronegative)



(B) Covalent Bond-

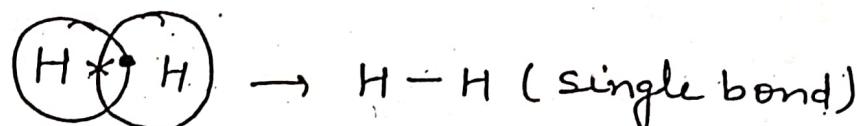
"A bond formed by mutual sharing of one or more electrons is known as covalent bond."

Covalent bond is formed between two electronegative atoms.

Covalent bond may be single (-), Double (=) or triple (\equiv) depending upon the fact whether one, two or three pairs of electrons are shared between two atoms.

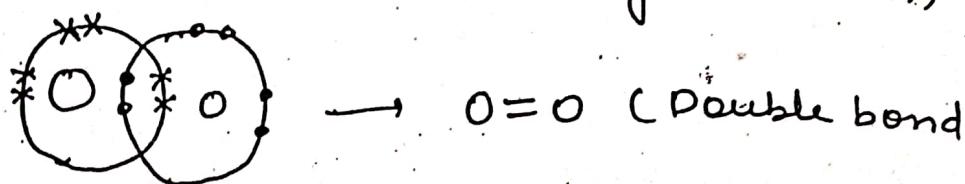
$1\text{H} - 1\text{s}^1$ (Electronegative atom)

$1\text{H} - 1\text{s}^1$ (Electronegative atom)



$8\text{O} - 1\text{s}^2, 2\text{s}^2, 2\text{p}^4$ (Electronegative atom)

$8\text{O} - 1\text{s}^2, 2\text{s}^2, 2\text{p}^4$ (Electronegative atom)



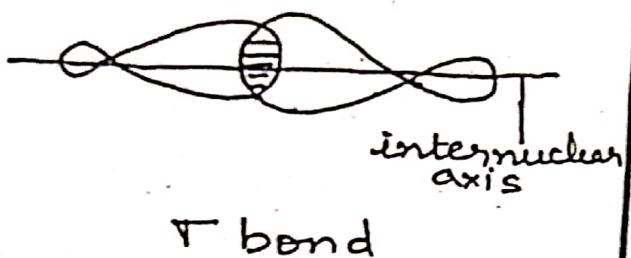
Covalent bond may be of two types-

(i) σ bond (Sigma Bond)

(ii) π bond (Pi-Bond)

Sigma (σ) Bond

- (1) Bond formed from end to end overlapping of orbitals are known as σ -bonds.



- (2) The extent of overlapping is maximum in σ -bond and hence stronger.

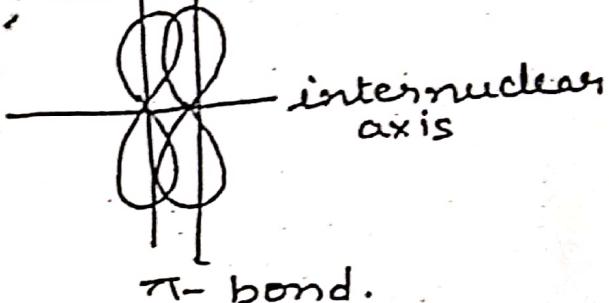
- (3) σ Bond is less reactive.

- (4) Electron density is maximum along the axes

- (5) σ bond determines the shape of the molecule.

Pi (π) Bond.

- σ -Bonds formed by lateral overlapping of orbitals are known as π -bonds.



- (3) The extent of overlapping is less due to lateral overlapping hence it is weaker than σ bond.

- (3) π -Bonds are more reactive.

- (4) Electron density is maximum above and below the internuclear axis.

- (5) π - bond does not affect the shape of the molecule.

Engineering Chemistry (RAS-102)Lecture No. 2(Molecular orbital theory)

Introduction - This theory was proposed by Hund and Mulliken in 1932.

- Molecular orbital theory explains-
- formation of molecular orbitals
- Magnetic behaviour of molecules.
- Bond order of molecules.
- Relative stabilities and Bond length of molecules.

Postulates of Molecular orbital theory -

- (1) According to Molecular orbital theory (MOT) Atomic orbitals (AO) overlap to form molecular orbitals (MO).
- (2) Atomic orbitals overlap according to linear combination of Atomic orbitals (LCAO) method.
- (3) Atomic orbitals loose their identity to form molecular orbitals.
- (4) Molecular orbitals are polycentric in nature i.e. there is influence of more than one nucleus.
- (5) Number of Molecular orbitals will be the same as the no. of combining Atomic orbitals.
- (6) 50% of molecular orbital form have less energy than combining Atomic orbitals, they are known as Bonding Molecular orbital.

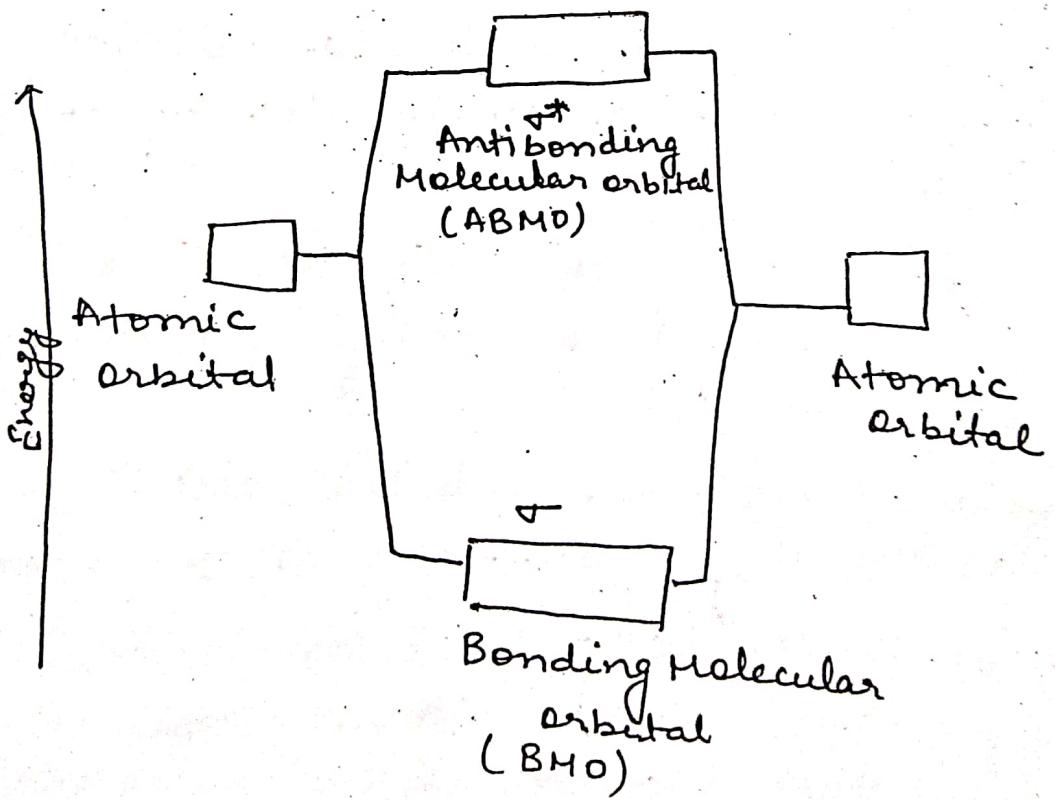
(7) Rest 50% of molecular orbitals have higher energy than combining Atomic orbitals, they are known as Antibonding Molecular orbital. They are represented by a * sign.

(8) The energy of orbitals will be as follows-

Bonding Molecular Orbital < Atomic < Antibonding orbital Molecular orbital.

(9) filling of electrons in molecular orbitals follows the same basic rules, which are followed by Atomic orbitals i.e. Hund's Rule, Pauli's exclusion principle, Aufbau principle.

(10) Representation of energy level diagram.



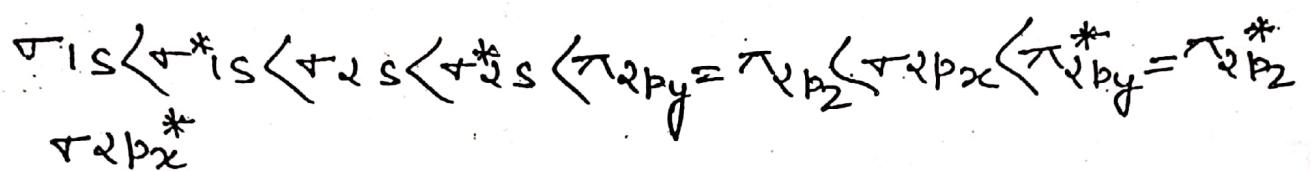
Engineering chemistry (RAS-102)Lecture NO.-3

(11)

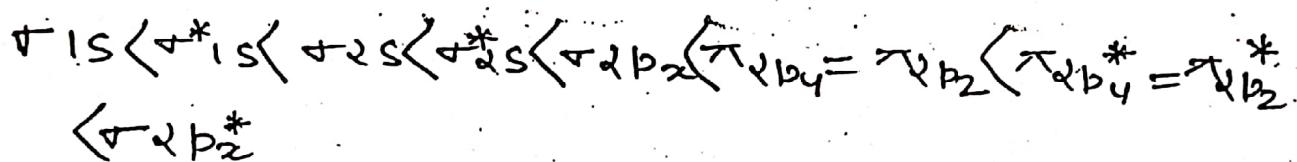
(Molecular orbital theory)Configuration -

Molecules are divided into two categories -

(A) Lighter Molecule (Molecule having upto 14 electrons)



(B) Heavier molecule (Molecules having Beyond 14 electrons)



(12) Bond order (B.O) - Bond order is equal to the number of covalent bond. from the configuration of Molecule bond order can be calculated according to following formulae -

$$B.O = \frac{1}{2}(N_B - N_A)$$

where N_B = No. of Bonding electrons

N_A = No. of Antibonding electrons

Bond order may be fractional or positive integer. But it cannot be zero or negative.

no bonding between two atoms.

(13) Bond order & Stability

(14) Bond order $\propto \frac{1}{\text{Bond length.}}$

(15) Bonding in Molecule can be represented by Energy level diagram.

C (16) From configuration magnetic behaviour of molecule can be explained. If in configuration there is any unpaired electron, then molecule will be Paramagnetic.

If all the electrons in molecular configuration are paired then the magnetic behaviour of molecule will be Diamagnetic?

* Questions Asked in University Exam.

Ques-1 Who propose Molecular orbital theory.

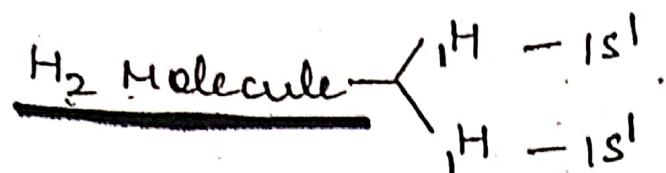
Ques-2 Differentiate between BMO and ABMO.

Ques-3 Define Bond order.

Ques-4. Explain the postulates of Molecular orbital theory.

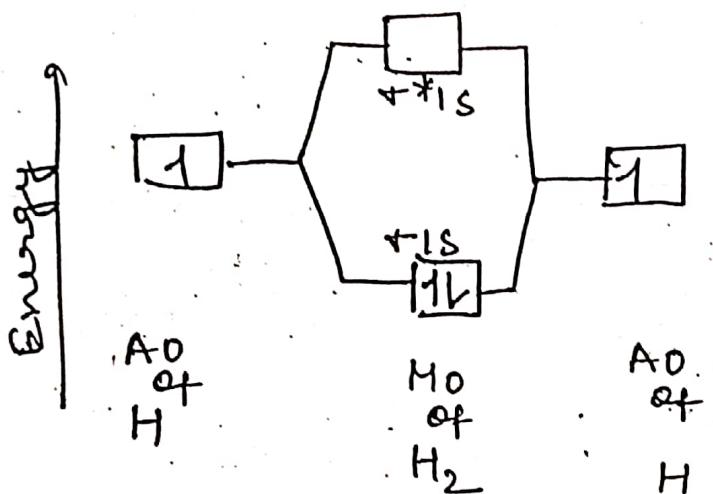
Eng. chemistry (RAS-102)Lecture No. 5

(Applications of MOT to homo-nuclear diatomic molecules)



Configuration - $\sigma_{1S}^2 \sigma_{1S}^0$

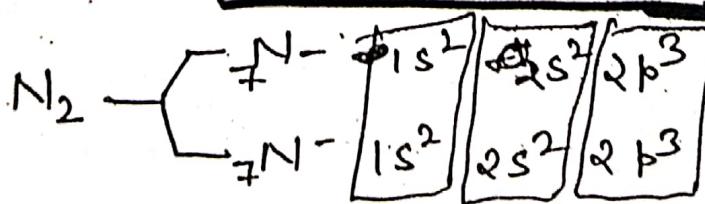
Energy level diagram -



Bond order

$$\begin{aligned}
 &= \frac{1}{2} [N_B - N_A] \\
 &= \frac{1}{2} [2 - 0] \\
 &= 1 \text{ (Diamagnetic)}
 \end{aligned}$$

N₂ - Molecule.

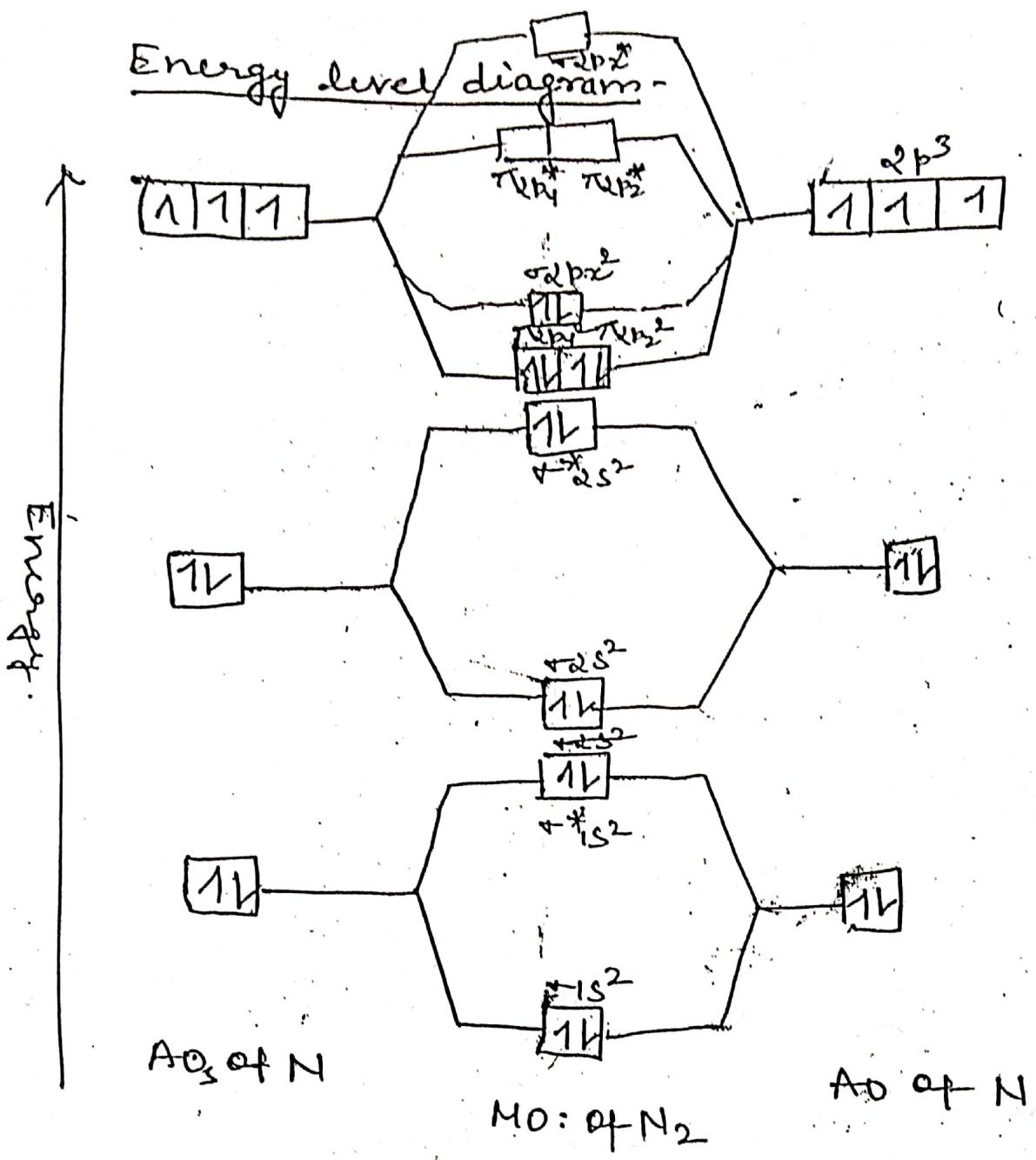


Total No. of e⁻ = 14
Lighter molecule

Configuration - $\sigma_{1S}^2 \sigma_{1S}^2 \sigma_{2S}^2 \sigma_{2S}^2 \pi_{2p_y}^2 \pi_{2p_y}^2 \pi_{2p_u}^0 \pi_{2p_u}^0 = \pi_{2p}^2 \pi_{2p_x}^2$

$$\pi_{2p_u}^0 = \pi_{2p_2}^0 + \pi_{2p_x}^0$$

Energy level diagram -

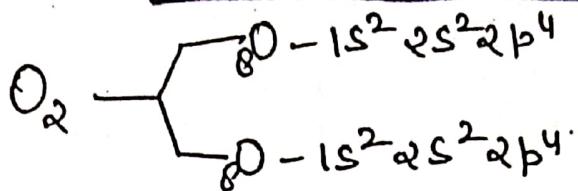


$$\begin{aligned} \text{Bond order} &= \frac{1}{2} [N_B - N_A] \\ &= \frac{1}{2} [10 - 4] \\ &= 3 \end{aligned}$$

Magnetic behaviour = Diamagnetic
(Due to all paired e⁻)

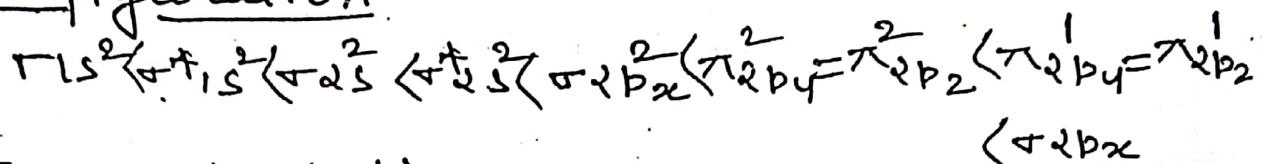
Applications
of MOT

O₂ Molecule

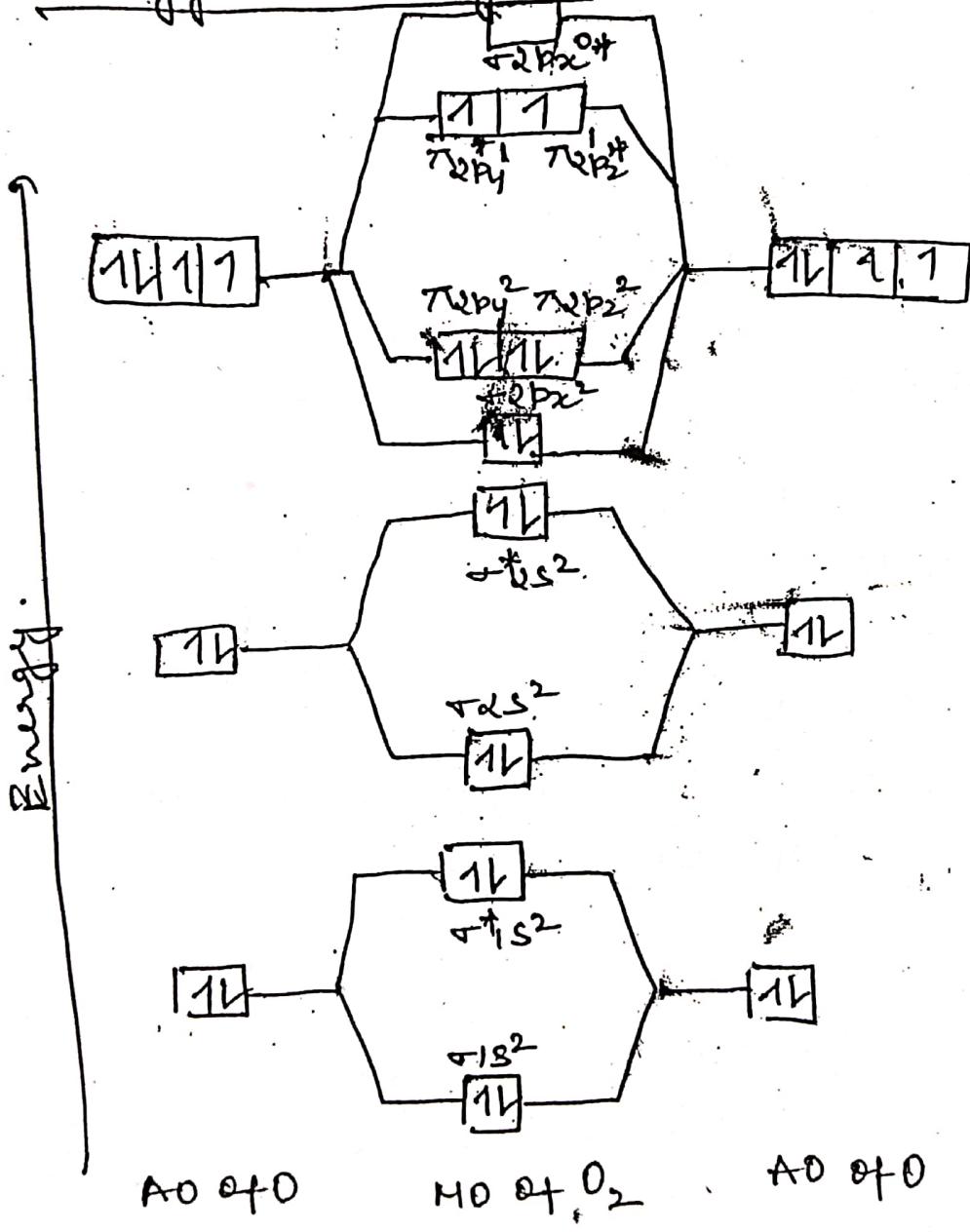


No. of electrons = 16 (heavier molecule)

Configuration -



Energy level diagram -



$$\text{Bond order} = \frac{1}{2} [N_B - N_A]$$
$$= \frac{1}{2} [10 - 6]$$
$$= \underline{\underline{2}}$$

Magnetic behaviour = Paramagnetic
(Due to unpaired
 e^-)

* Questions asked in University examination.

Ques-1 Explain MOT with the example of N_2 and O_2 . [2015-16 even sem]

Ques-2 - Arrange H_2 , N_2 , O_2 in decreasing order of stability.

Ques-3 Explain the paramagnetic behaviour of Oxygen according to MOT.

Molecular Orbital diagram for Hetero-nuclear diatomic Molecules:

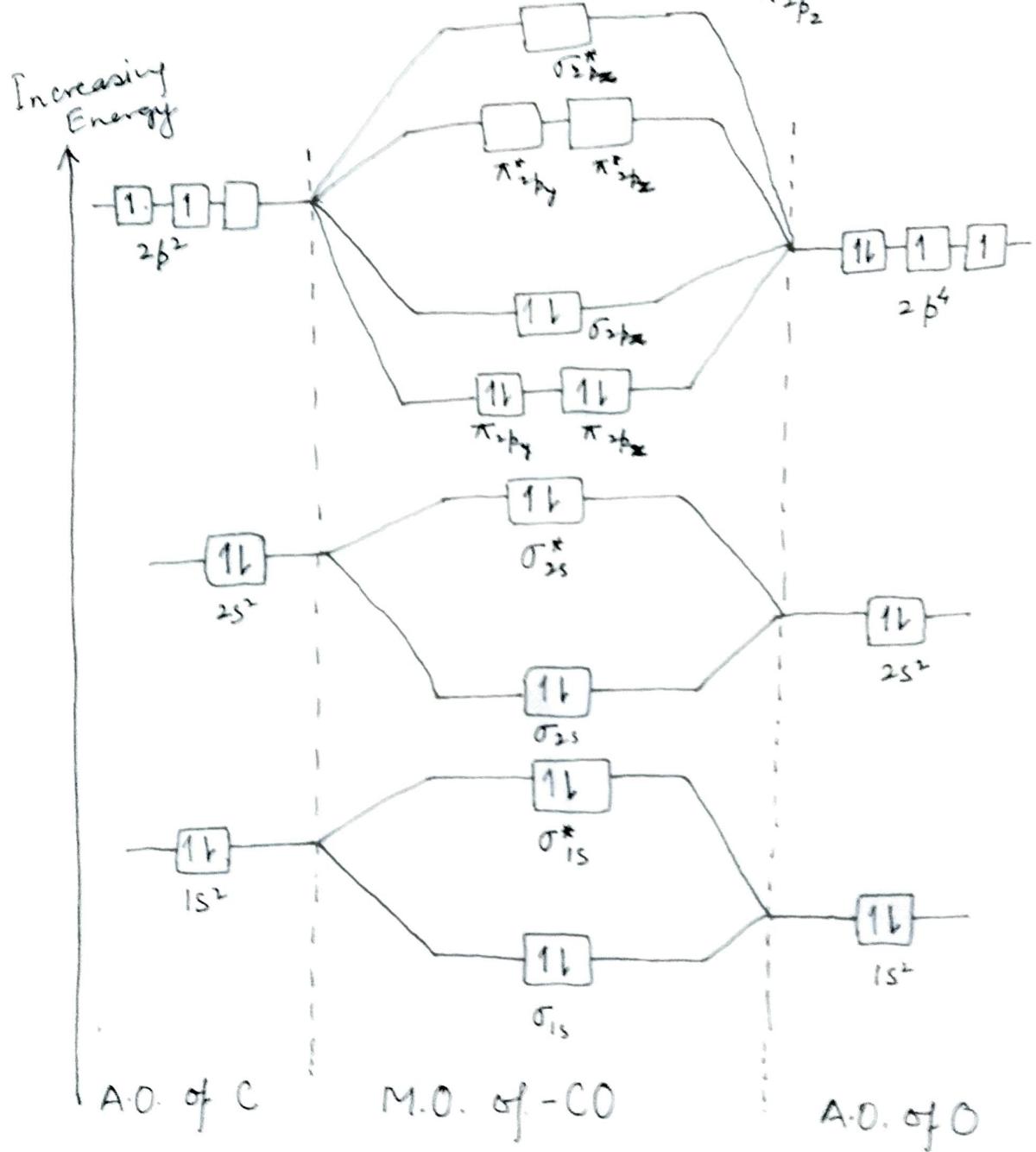
The molecular orbital diagram of heteronuclear diatomic molecules is not symmetrical as those of homonuclear ones. Because in this case the electronegativities of the corresponding atoms are different.

In these cases the energy level of more electronegative atom is slightly lower than less electronegative atoms.

CO molecule :

$$\text{No of electrons} = 6(\text{in - C}) + 8(\text{in - O}) = 14$$

configuration :- $\sigma_{1s^2}, \sigma_{1s^2}^*, \sigma_{2s^2}, \sigma_{2s^2}^*, \left\{ \begin{array}{l} \pi_{2p_y}^2 \\ \pi_{2p_z}^2 \end{array} \right. \sigma_{2p_x}^2$



$$\text{B.O.} = \frac{10-4}{2} = \frac{6}{2} = 3 \quad \text{hence it is a stable molecule}$$

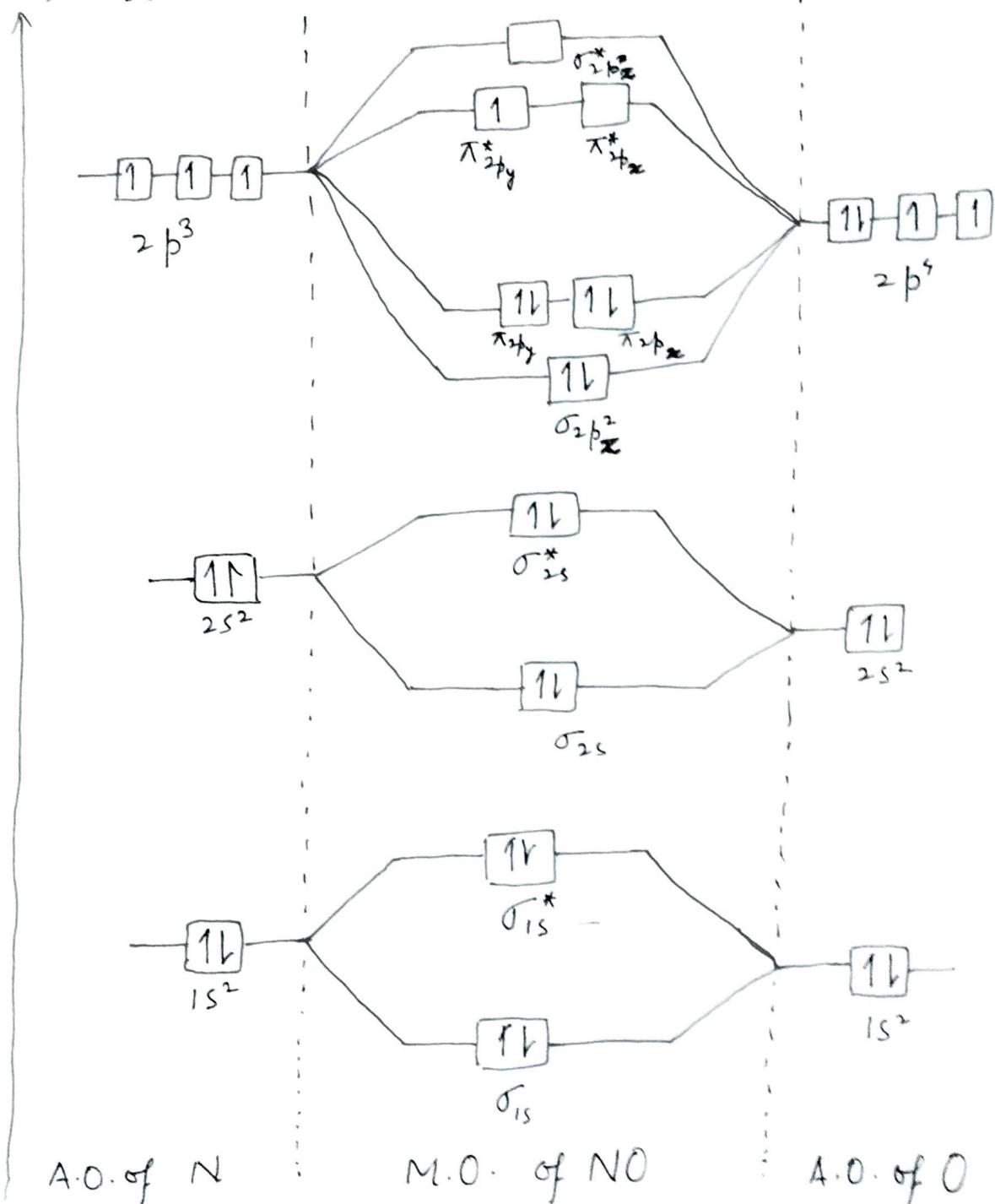
It has no unpaired electron hence it is diamagnetic in nature

NO - molecule :

$$\text{No of electrons} = 7(\text{in-N}) + 8(\text{in-O}) = 15$$

Configuration $\Rightarrow \sigma_{1s^2}, \sigma_{1s^2}^*, \sigma_{2s^2}, \sigma_{2s^2}^*, \left\{ \begin{array}{c} \sigma_{2p_x^3} \\ \sigma_{2p_y^2} \\ \sigma_{2p_z^2} \end{array} \right\}, \left\{ \begin{array}{c} \pi_{2p_y^2} \\ \pi_{2p_z^2} \end{array} \right\}, \left\{ \begin{array}{c} \pi_{2p_x}^* \\ \pi_{2p_y}^* \end{array} \right\}$

Increasing Energy



A.O. of N

M.O. of NO

A.O. of O

$$\text{B.O.} = \frac{10 - 5}{2} = 2.5$$

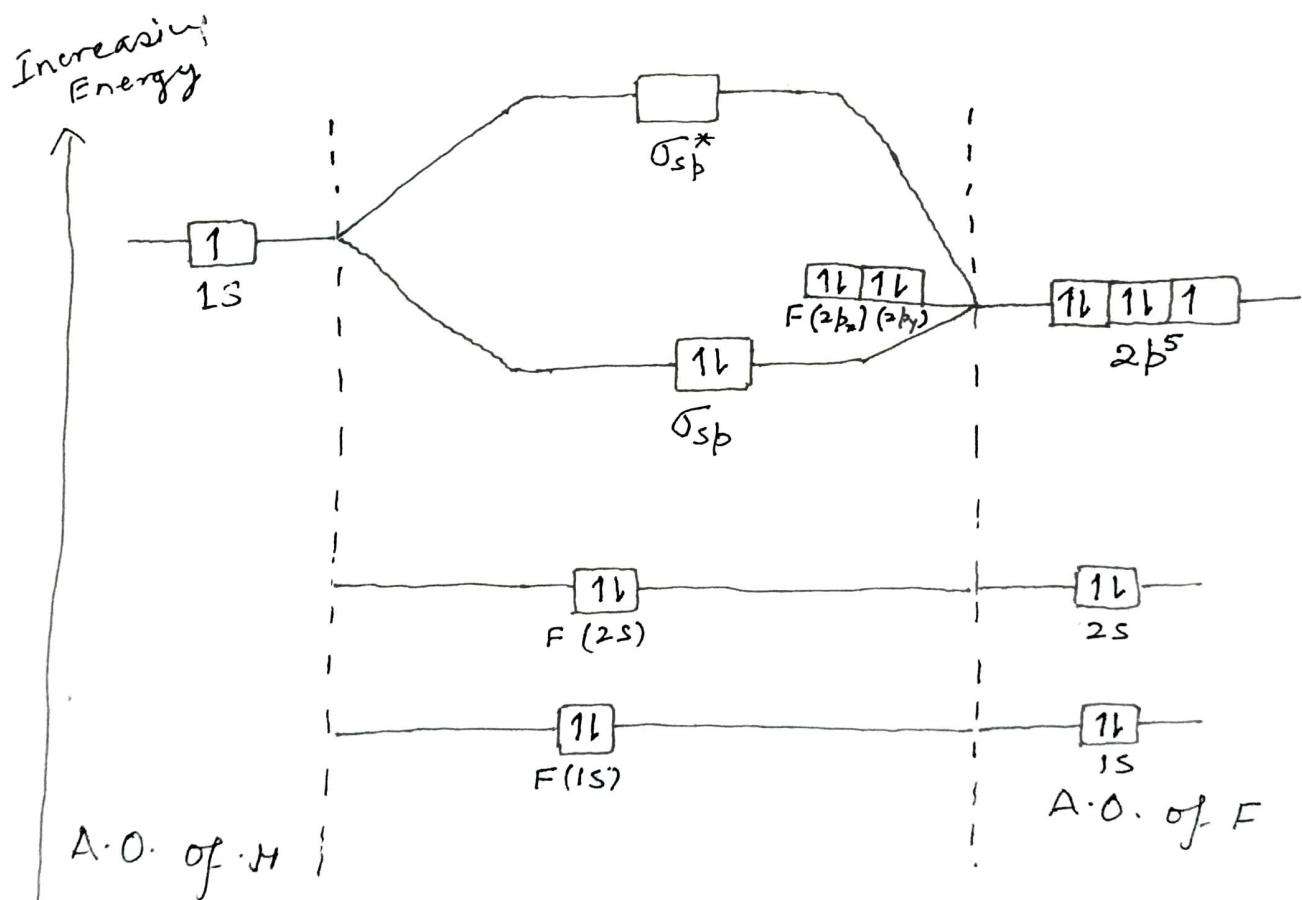
It has one unpaired electron hence it is paramagnetic in nature.

HF - molecule:

$$\text{No of electrons} = 1 \text{ (in -H)} + 9 \text{ (in -F)} = 10$$

$$\text{Configuration} = 1S^2, 2S^2, 2p_x^1, 2p_y^1, [6_{sp}^2], 2p_z^2, 2p_y^2$$

In the formation of HF molecule s-orbital of hydrogen overlaps effectively only with $2p_z$ orbital of Fluorine hence resulting into only one 6_{sp} orbital and corresponding 6_{sp}^* -orbital. The remaining electrons of F don't participate in bond formation. Hence M.O. diagram of HF molecule will be as follows -



$$\text{B.O.} = \frac{2-0}{2} = 1$$

It has no unpaired electron hence it will be diamagnetic in nature.

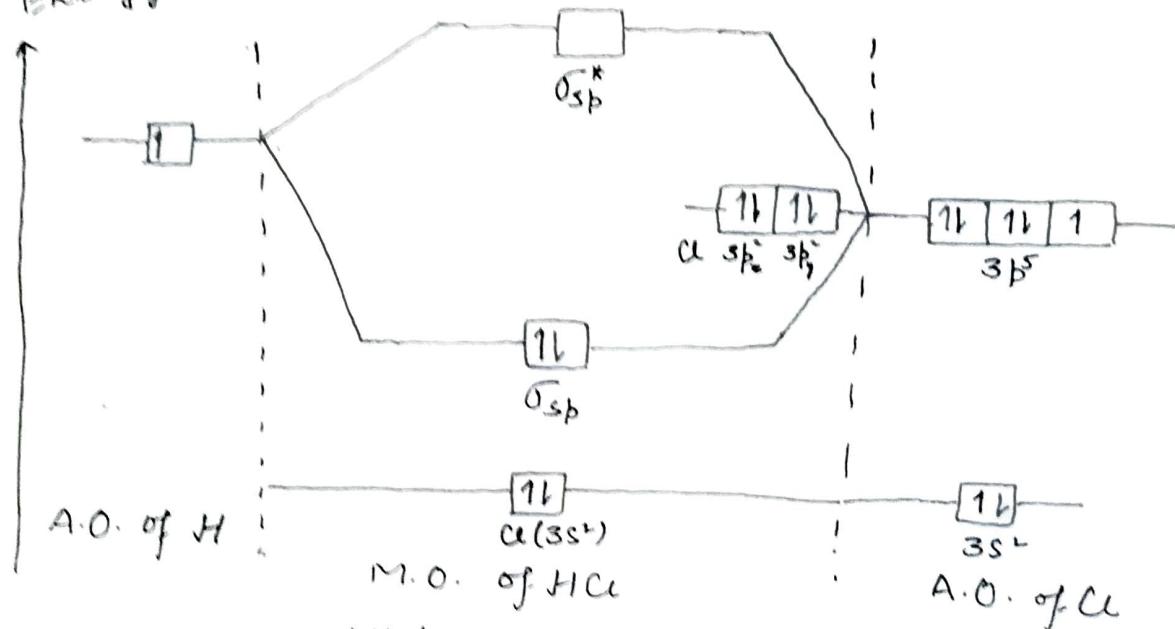
HCl - molecule :

No of electrons = 1 (in-H) + 17 (in-Cl) = 18

Configuration = $1s^2, 2s^2, 3s^2, 3p_0^2, 3p_x^4, 3p_y^2$

In the formation of HCl-molecule, s-orbital of hydrogen overlaps effectively with only $3p_z$ orbital of chlorine hence resulting into one $3p$ -bonding molecular orbital & corresponding bonding $3p^*$ -A.B.M.O. Rest electrons don't participate in bonding hence M.O. diagram of HCl will be as follows-

Increasing Energy



$1s$ & $2s$ orbitals of -Cl is not shown due to simplicity.

$$B.O. = \frac{2-0}{2} = 1$$

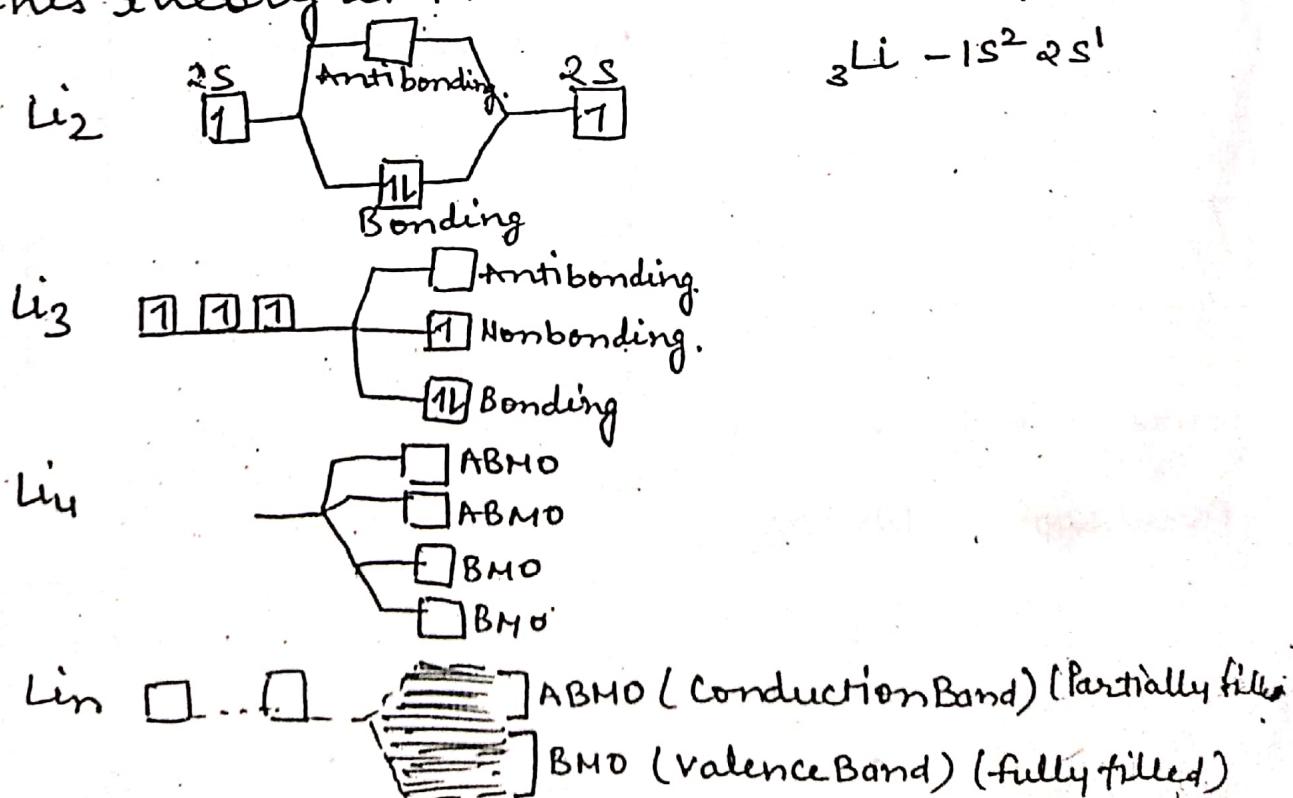
In this case there exist no unpaired electron hence HCl is diamagnetic in nature.

(Band theory of solids)

Introduction- Band theory is the explanation of metallic bonding (i.e. bonding between two metals) according to MOT.

Various properties of metals ~~were~~ cannot be explain with the help of electron sea model, so there is a need of new theory to explain metallic bonding. A/c to MOT, all properties of metals can be explained.

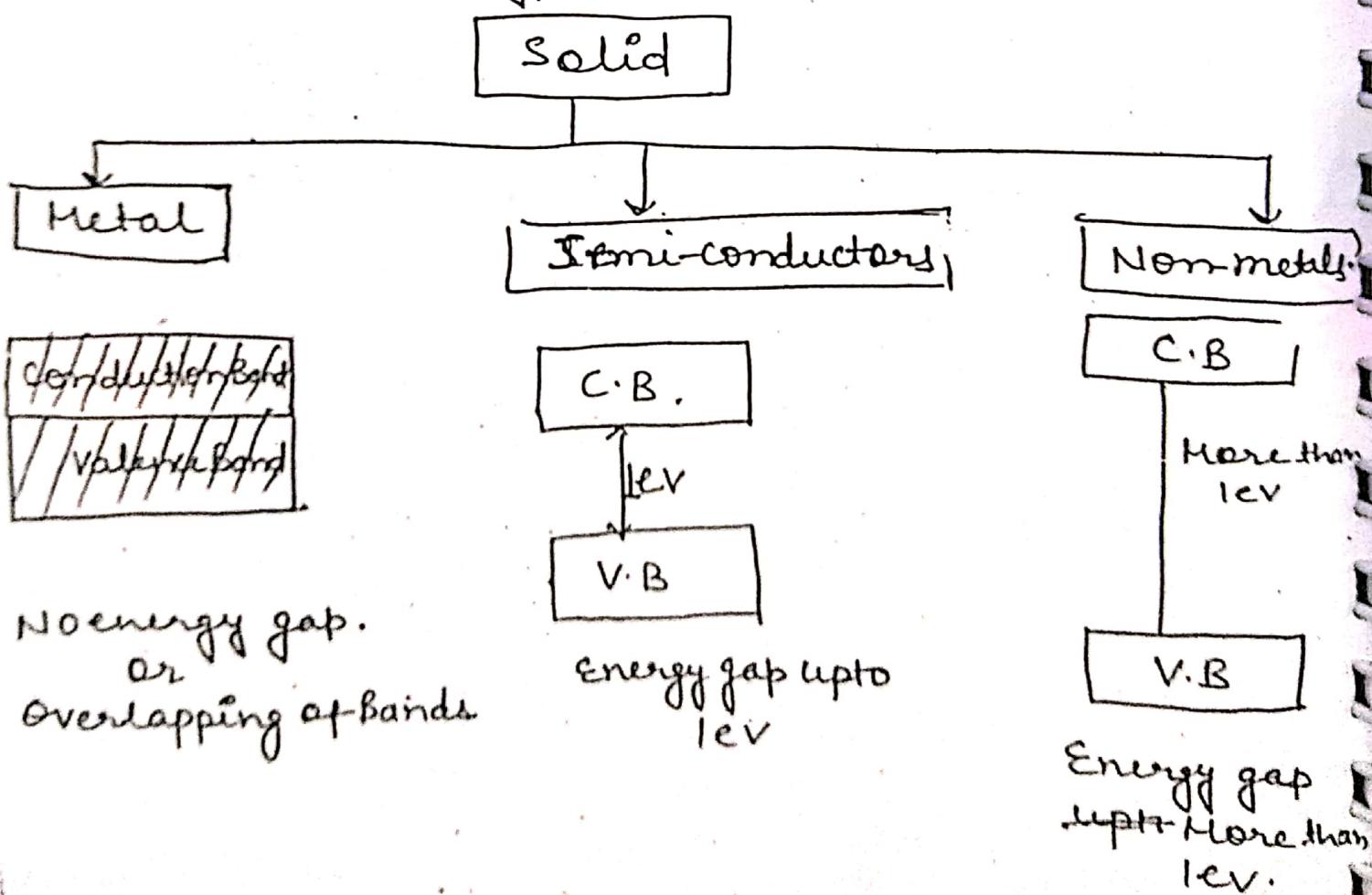
According to MOT, the no. of molecular orbital same as the no. of combining AOs. When 10^{23} (Avogadro's NO.) AO overlap then the no. of MOs will also be 10^{23} . When there will be so many MOs, then there energy separation will be too less, & they looks like a band. That's why this theory is known as Band theory.



As we know alc to MOT 50% of formed MO will have less energy and they are known as BMO. They are generally fully filled or partially vacant. When valency electrons come into BMO, that's why BMO of solids are also known as 'Valence Band'.

While rest 50% of MOs have higher energy than combining AOs, they are generally fully vacant or partially filled. They are known as 'Conduction Band'. The energy difference between Valence Band and Conduction band is known as 'Forbidden Band' or 'Energy gap'. These bands of molecules are also known as 'Quasi-continuous Band'.

Depending on Energy gap solids are of three types -



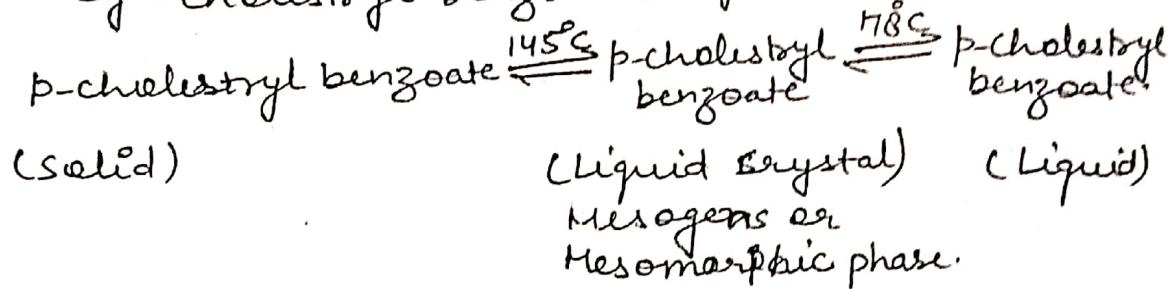
Eng. Chemistry (RAS-102) " "
(Lecture NO. 7)

(Liquid Crystal)

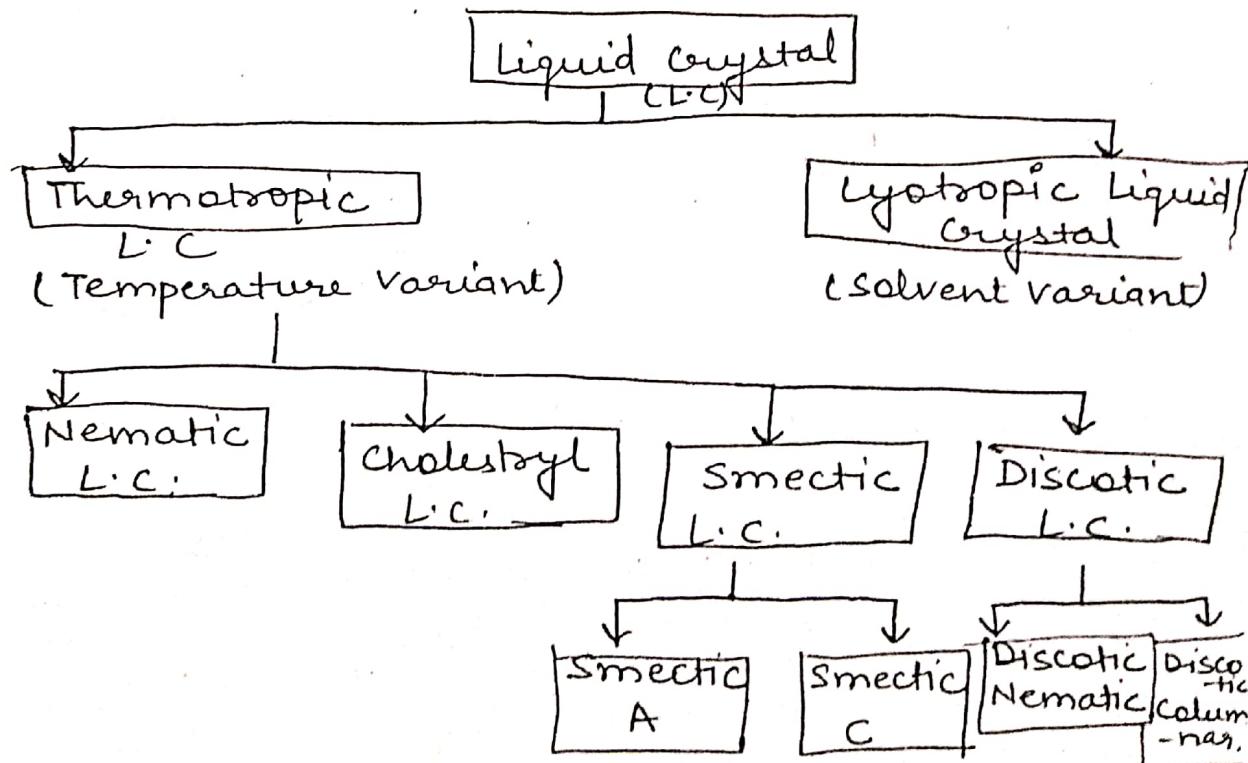
"Liquid crystals are the substances that exhibit a phase of matter that has properties between those of a conventional liquid and a solid crystal." ... always like a liquid

A liquid crystal may flow like a liquid and have arrangement of molecules like a crystal.

Eg. Cholesteryl benzoate, glycolipids, surfactants.



Classification of Liquid Crystal -



Both types of liquid crystal i.e. thermotropic and lyotropic liquid can be explain on the basis of orientational order and positional order.

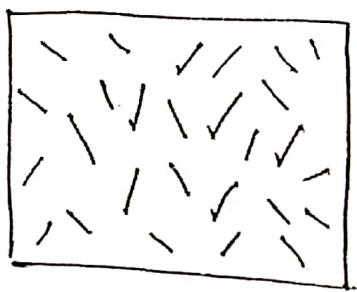
Positional order - Positional order may be defined as the tendency of molecules to occupy fixed positions.

orientational order - It may be defined as the tendency of molecules to orient in a particular direction.

Various types of liquid crystal on the basis of orientational order and positional order are as follows -

(1) Nematic Liquid Crystal or Thread like liquid crystal -

These crystal lack of positional order, but have orientational order. They are thread like and temperature sensitive.
e.g. β -azoxyanisole.



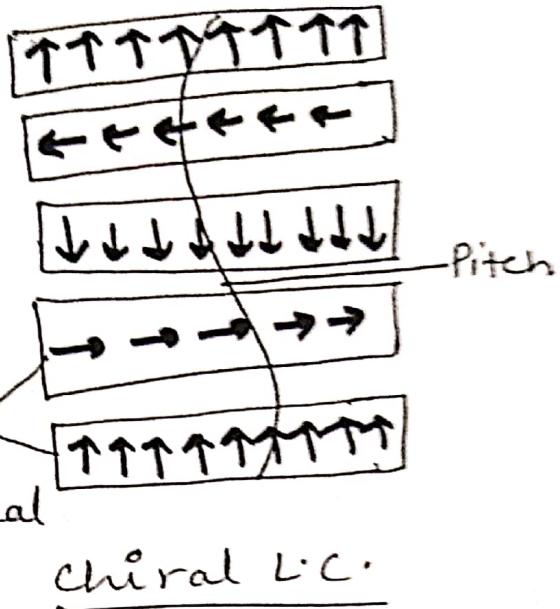
• Nematic L.C.

(2) Cholesteryl or chiral liquid crystal -

cholesterol itself is not a example of L.C. but their derivatives are the example of chiral L.C. All over in cholesteryl liquid crystal there is no orientational order and no positional order but layer-wise there are positional and orientational order.

The molecules in successive layers are slightly twisted or rotated with respect to the layers above and below so as to form a continuous helical or spiral pattern.

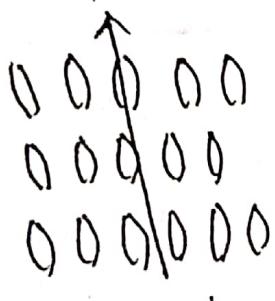
Layerwise orientational and positional order.



Pitch is an important characteristic of the mesophase and may be defined as the distance taken by the director or rotate on full turn (360°) in the helix. Eg. cholesterol derivatives. They are highly temperature sensitive.

(3) smectic liquid crystal - The molecules in smectic crystals are

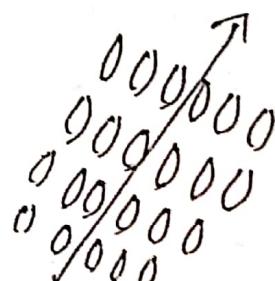
oriented parallel to each other. There are some amount of orientational order and some amount of positional order. They are 'soaplike' i.e they are present in layers.



Smectic-A

Molecules are aligned perpendicularly to the layer planes.

Eg. Ammonium oleate.



Smectic-C

Director is twisted in a particular direction

(4) Discotic Liquid crystal -

They are Disc like (discotic nematic) and plate like (discotic columnar)

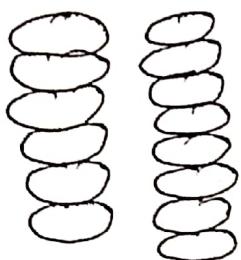
Discotic Nematic



They have orientational order but no positional order like equidistant coins.

Eg. Benzene hexalkanoids.

Discotic columnar



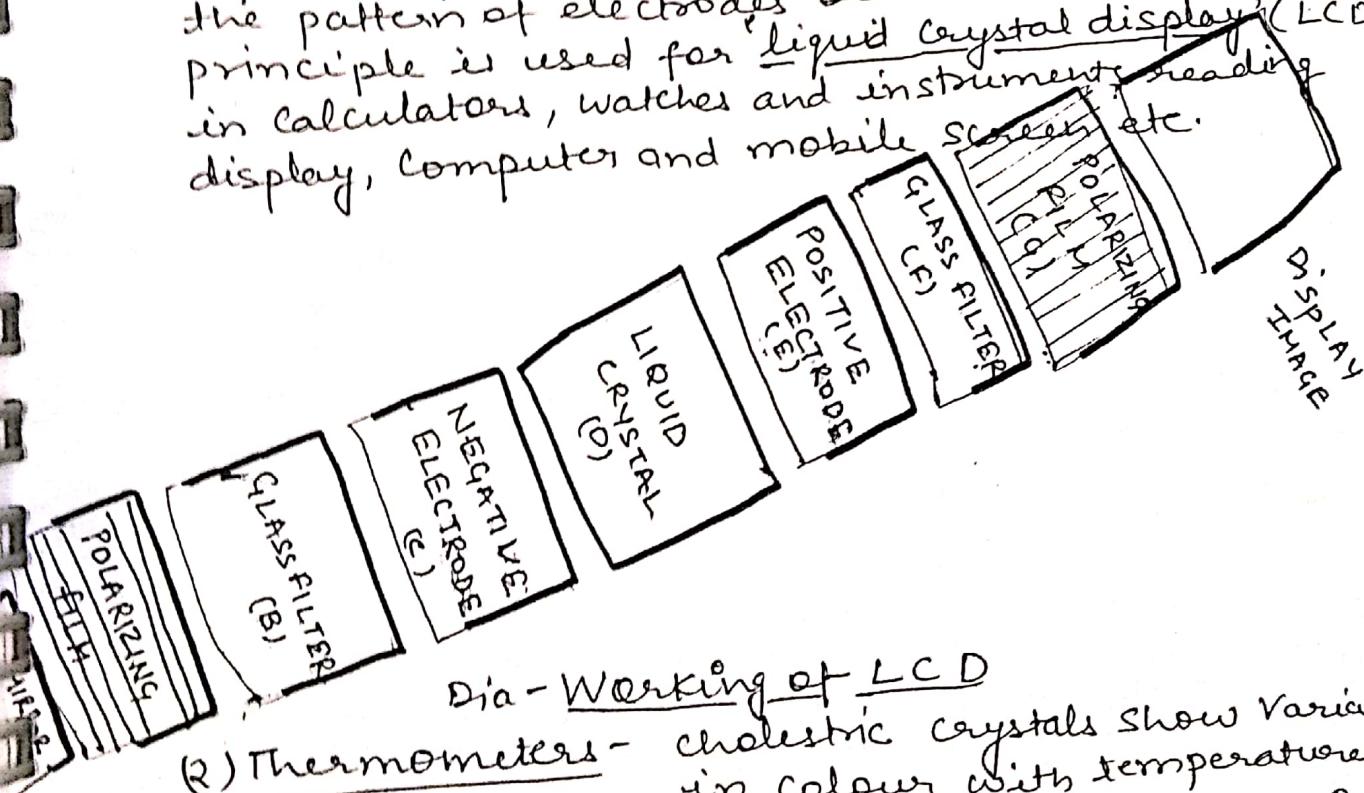
They have orientational as well as positional order. They are arranged in hexagons as well as in columns.

- * Question asked in University examinations-
- Ques-1 - Define liquid crystal with example.
 - Ques-2 - Define the term liquid crystal and give their classification.
 - Ques-3 - Briefly explain various types of liquid crystals.

(Applications of liquid crystal)

Liquid crystals have widespread applications in the field of science and technology. Their anisotropic optical properties make them very useful in various devices. Liquid crystal have following applications -

(1) In Display - Orientation of nematic liquid crystal is easily changed by electric field or pressure and the changed orientation have different light transmission and reflection e.g. when an electric field is applied, on thin liquid crystal film with the help of electrodes, the pattern of electrodes become visible. This principle is used for liquid crystal display (LCD) in calculators, watches and instruments, reading display, computer and mobile screen etc.



Dia - Working of LCD

(2) Thermometers - cholesteric crystals show variation in colour with temperature. These crystals are highly sensitive for change of temperature and show specific colour at particular temperature. They are able to record the

change of 0.01°C temperature variation.

(3) Radiation and pressure sensors - The colour changing ability of cholesteric crystals with temperature finds use in radiation and pressure sensors.

(4) optical imaging - cholesteric liquid crystals are used in optical imaging.

(5) In research work, Nematic liquid crystal is used

(6) In thermography, liquid crystals are used.

(7) lyotropic liquid crystals are used in household soaps. They help in removing residual oil

(8) In medical field, certain drugs are coated with lyotropic liquid crystal.

* Questions asked in university examination

Ques-1. Explain the application of liquid crystal in display

Ques-2 - Explain liquid crystal with their applications.

Engineering Chemistry (RAS-102)Lecture NO-9(Point Defect)

"Any deviation from an ordered and periodic arrangement is known as crystal imperfection."

Crystal imperfections have strong influence upon many properties of crystals, thus some properties of crystal such as strength, conductivity, are controlled by as much as by imperfections and by nature of the host crystals.

- Conductivity of some semi-conductors is due to chemical impurities
- Colour of many crystals arises from impurities and imperfections.
- Mechanical and plastic properties are controlled by imperfections.

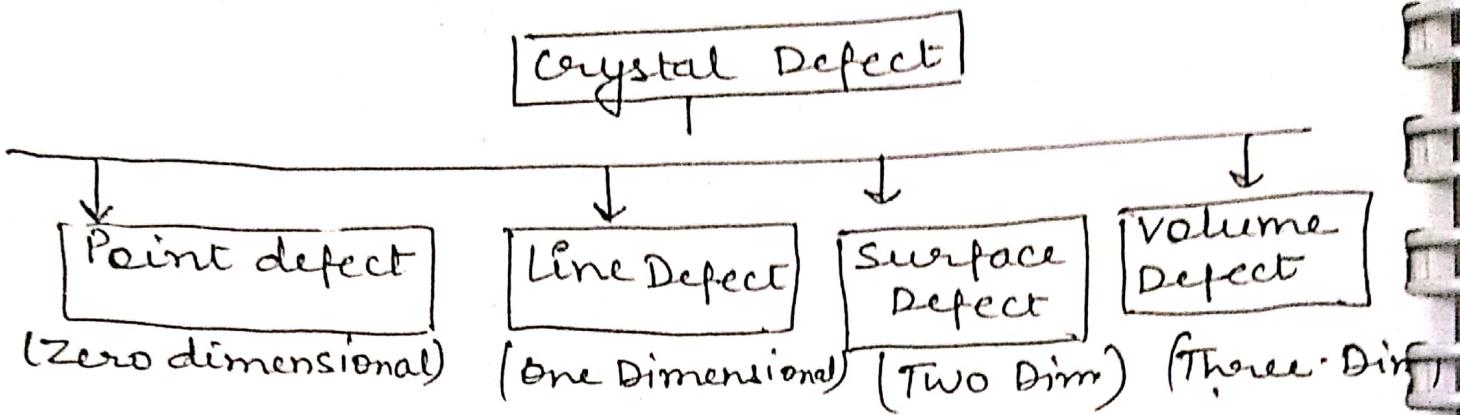
Defects may be of two types-

- (i) stoichiometric defect
- (ii) Non-stoichiometric defect.

Stoichiometric defects are those defects which obey the law of constant composition i.e. cation and anion ratio does not change after imperfect ion.

Non-stoichiometric defects are those defects which does not obey the law of constant composition i.e. the ionic ratio changes after imperfection.

Types of Crystal Defect



Point Defect

↓
Vacancy Defect

Eg. Schottky Defect
→ when an ion leave its space to create vacancy.

↓
Substitution Defect

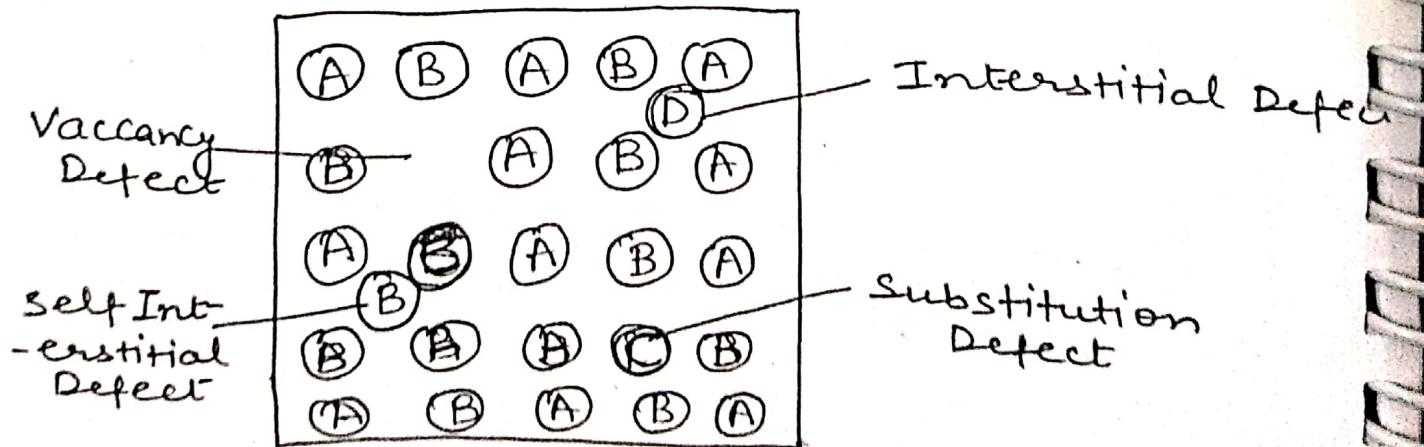
→ when a foreign ion replaces host ion.

↓
Interstitial Defect

Eg. Frankel Defect
→ when ions leave their space and settle in interstitial space of solids.

↓
Self Interstitial Defect

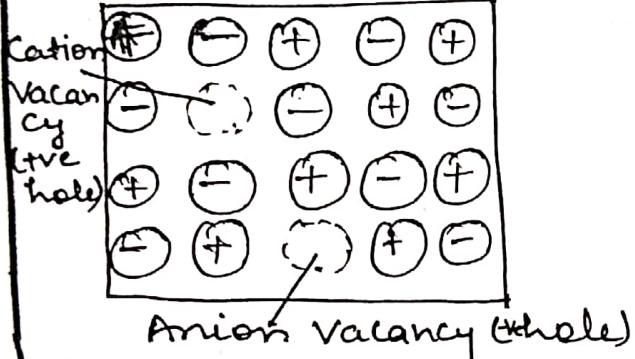
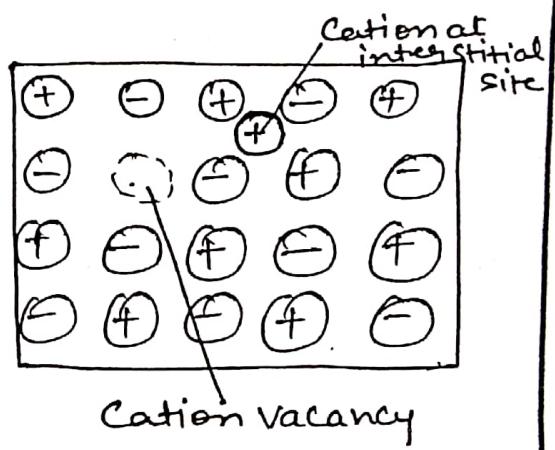
Eg. Frankel Defect
when ions leave their own space and settle in interstitial space.



Dia - showing various Point defects.

There are two examples of ~~points~~ Defects

- (1) Schottky Defect (2) Frankel Defect.

Schottky Defect	Frankel Defect
<p>(1) When an positive ion and negative ions are missing from any site in crystal lattice, then a pair of holes are created. This defect is known as Schottky Defect.</p> 	<p>When an ion (generally +ve) shifts from its position to interstitial position, then a vacancy or hole is created, this is known as Frankel defect.</p> 
<p>(2) The Schottky defect is generated by ionic crystal when</p> <ul style="list-style-type: none"> → co-ordination no. of an ion is high → when the size of anions and cations are almost equal. 	<p>(B) This defect can occur in ionic crystals when</p> <ul style="list-style-type: none"> → The anion is much larger than size of cation → The ion has low co-ordination no.
<p>(3) Density decrease in Schottky defect</p>	<p>(B) Density remains same generally.</p>
<p>(4) Electric conductivity increases due to holes</p>	<p>(C) Conductivity slightly increases.</p>

- | | |
|---|--|
| (5) Holes are of both types (+ve and -ve) | (5) Holes are only one types (generally +ve) |
| (6) This is stoichiometric Defect. | (6) This may be stoichiometric or Non-stoichiometric |

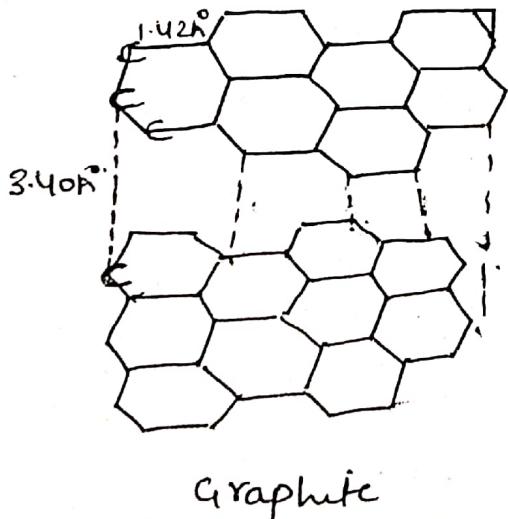
* Question asked in University Examinations-

- Ques-1 Explain the term imperfection in crystal.
- Ques-2- Explain Point defects.
- Ques-3 - Differentiate between Schottky and frankel defect.

(Structure and Applications of Graphite and fullerenes)

Graphite- Graphite is the allotrope of carbon.

Structure- In Graphite C-atoms are arranged in the form of hexagons and hexagons are arranged in layer. In Graphite structure C-atom is attached with 3 C-atom, in which 2-C-atoms are of same hexagon while 3-Carbon is of another layer hexagon. Layers are attached with the help of weak Vander waals forces. Distance between two adjacent C-atoms are 1.42 \AA while distance of C-atoms of two different layers are 3.40 \AA .



In Graphite each C-atom is sp^2 -hybridized.

Conducting Property -

As C-atoms in Graphite are sp^2 hybridized due to which there is availability of one p-orbital, which is vacant. That's why Graphite show conductivity.

Lubricating Property - In Graphite two layers of hexagons are attached with the help of weak Vander Waal's forces, due to which layers are slippery as

flexible in nature. That's why Graphite shows lubricating Property.

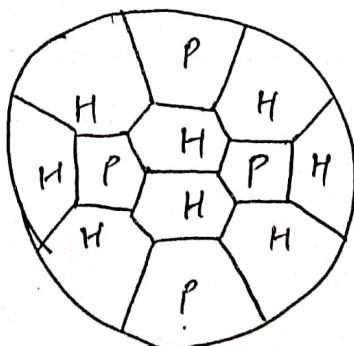
Applications of Graphite -

- (1) Graphite is used as conductor. in batteries.
- (2) Graphite is used as lubricating agent.
- (3) In Reaction Vessel
- (4) In Metallurgical crucible.
- (5) In electrodes.
- (6) Graphite is used in Nuclear Reactors

Fullerene or C₆₀

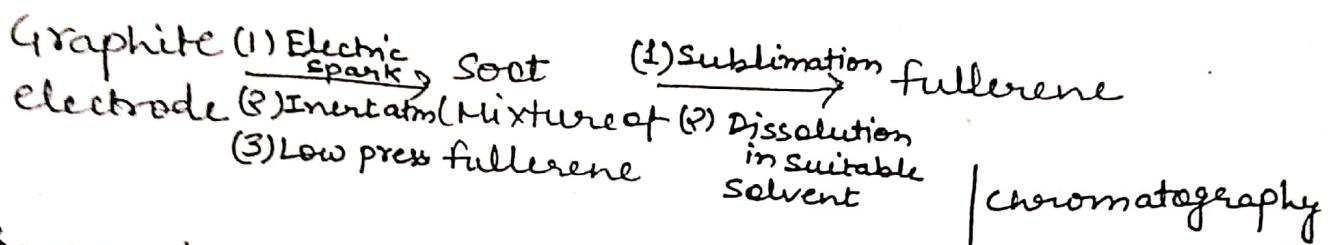
Fullerene is the third allotrope of carbon.

Structure - Fullerene is soccer ball like structure which is hollow from inside. This is polymorphic in nature i.e. more than one type of shapes are present in it. In fullerene carbon are present in the form of hexagons and pentagons. And hexagons and pentagons are arrayed in that way that two hexagon can share a common wall but two pentagon never share a common wall. Generally it contains 20 hexagons and 12 pentagons.



Fullerene is discovered by R. Buckminster Fuller. C₆₀ is first isolated fullerene but now C₃₂, C₈₀, C₇₀ has also been isolated.

Preparation of fullerene - When an electric spark is struck between graphite electrodes, then a black dust, in which the mixture of fullerene (35%). which is extracted by which we obtain 5-15% fullerene.



Properties of fullerene -

- (1) In C_{60} each Carbon is sp^2 - hybridized.
- (2) It is mustard colour solid.
- (3) Smaller atoms like alkali metals may occupy the hollow cage. The structure thus obtained is known as 'endohedral structure'. On the other hand if the radicals are attached outside the hollow cage 'exohedral structure' is obtained.
- (4) Some of the compounds of fullerene possess remarkable property of super-conductors.

Applications -

- (1) In making superconductors
- (2) Making soft ferrromagnets.
- (3) In electronic devices and optical (non-linear) devices.
- (4) Because of size, stability and hydrophobic nature, used as diagnostic agent.
- (5) Potential inhibitors of HIV

Concepts of Nano-materials and its applications.

Nanotechnology may be defined as -

"The application of science and scientific knowledge, at the nanoscale, for industrial or commercial objective."

"^{or}
The engineering of functional systems at the molecular scale."

The design, characterization, production and application of structures, devices and systems by controlled manipulation of size and shape at the nanometer scale (10^{-9} m) that produces superior functions or property of the device or system.

Nanomaterials are those substances which are of 10^{-9} m scale.

Methods for the Preparation of Nano-materials-

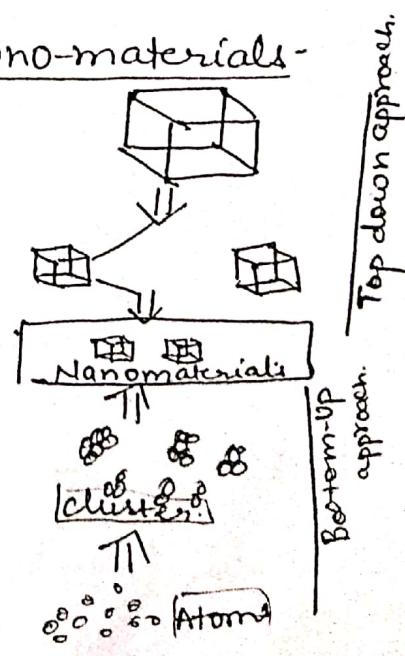
(A) Top-down Approach -

In this method small features are created on large substance by repeated pattern transfer steps.

This method is used in micro-electronic industry.

(B) Bottom-up Approach - This method

Starts with very small units, often individual molecules or atoms



and assemble these building-block units into larger structures.

Properties of Nanomaterials

Effects

Varying Properties.

Size effect

- Melting point, solubility, colour, transparency, catalytic behaviour,

Composition effect - Different physical and chemical behaviour of the material.
Observed by varying - Particle composition.

Surface effect -

Dispersibility, conductivity, catalytic behaviour, optical properties.

Applications of Nanomaterials-

(1) In Diagnosis - Gold nanoparticles tagged with DNA segment used for detection of genetic sequence in sample.

(2) Drug Delivery - used for delivering drug to specific cell.

(3) Energy -
→ Reduction of energy consumption,
→ increasing the efficiency of energy production, nuclear energy cleanup & waste storage.

(4) Information & Communication -

→ Memory storage.

→ Display of various devices, etc.

- (5.) food safety (Nano-sensors and nano tracers)
- (6.) Agriculture (Nano particles and nano emulsions in pesticides)
- (7) food processing (Nano-capsules)
- (8.) food Packaging (Smart Packages with oxygen sensors)
- (9) Helps in using more eco-friendly energy systems.
- (10) It provides better insulator systems.

* Questions asked in university examination-

- * Describe properties and applications of Nanomaterials.
- * Define the term nanomaterials and nano-technology.