

- * Chemical Bonding: the force of attraction that binds the atom within a molecule
- * Valence Bond Theory: was proposed by Heitler & London in 1927 and later developed by Pauling
Salient features of this theory are:-
 - Covalent bond is formed by the overlapping of half-filled atomic orbitals of different atoms
 - The overlapping electronic orbitals must have electron with opposite spin
 - The inner ~~orbital~~ orbitals from each atoms remain undisturbed
 - The strength of covalent bond depends upon the extent of overlapping. Greater the overlapping stronger is the bond formed.
 - Depending upon the type of overlapping, covalent bond may be divided into 2 types σ bonds and π bonds.

Drawbacks of VBT

- It was unable to explain the colourisation of elements.
- It did not explain the magnetic behaviour of the element
- It did not explain the complex formation

* Molecular Orbital Theory was given by

Hund & Mulliken in 1932.

Postulated / salient feature of MOT are :-

- The atomic orbital of the combining atom overlap and form molecular orbitals
- The number of molecular orbital formed is equal to the number of atomic orbitals involved in their formation
- This theory is based on wave mechanics
- The filling of electron in molecular orbitals is same as that in atomic orbitals (Pauli, Aufbau and Hund)

* Linear Combination Of Atomic Orbitals.

Acc. to this, linear combination of atomic orbitals can take place by addition and by subtraction of the wave function of atomic orbitals involved.

* For effective overlap combining atomic orbitals should have same energy and same symmetry

For eg. $\rightarrow H_2$

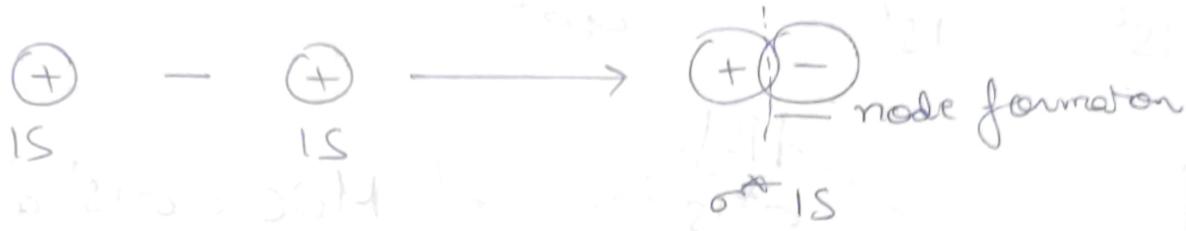


$$\Psi_A \quad \Psi_B \quad \Psi_{AB}$$

$$\Psi_A \pm \Psi_B \longrightarrow \Psi_{AB}$$

$$\Psi_A + \Psi_B \longrightarrow \Psi_{AB} \text{ (Bonding Molecular Orbital)}$$

$$\Psi_A - \Psi_B \longrightarrow \Psi_{AB}^* \text{ (Antibonding Molecular Orbital)}$$



Diff. b/w bonding and anti-bonding.

→ energy is less

→ stability is more

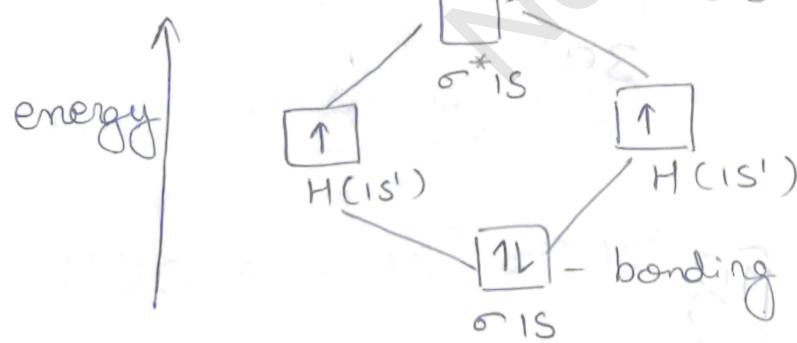
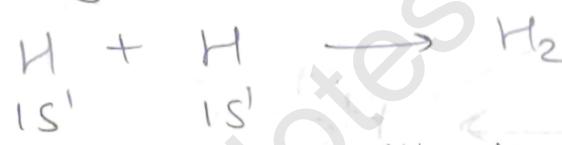
→ density is more

→ energy is more

→ stability is less

→ density is less

for hydrogen molecule, H_2

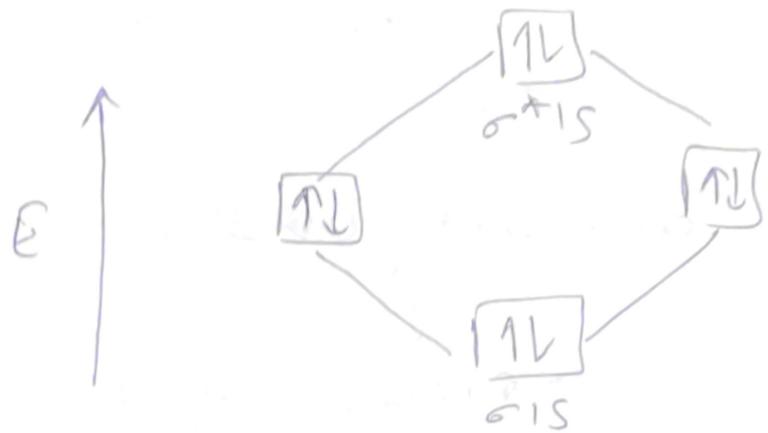
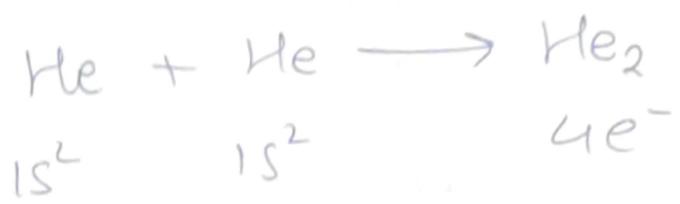


$$\text{MOC} = \sigma \text{IS}^2 \sigma^* \text{IS}$$

$$\text{Bond Order} = \frac{\text{Nb} - \text{Na}}{2} = \frac{2 - 0}{2} = 1$$

Diamagnetic because of paired electrons.

② He_2

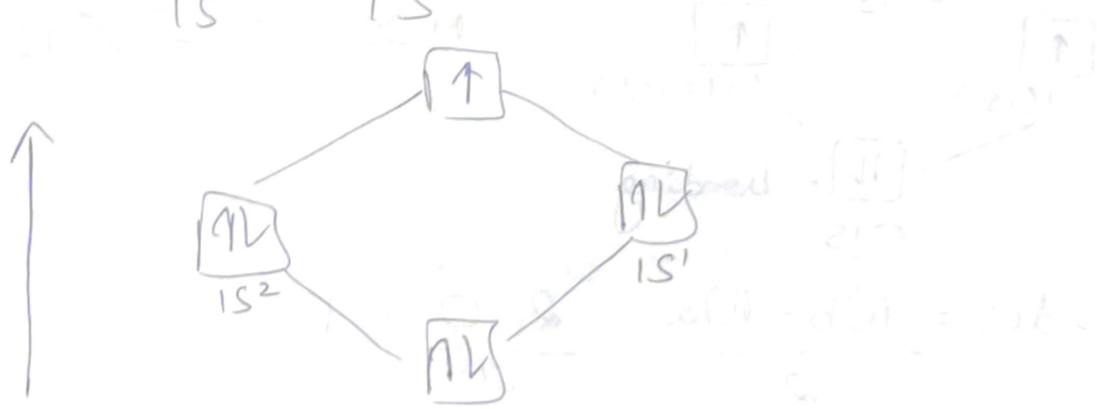
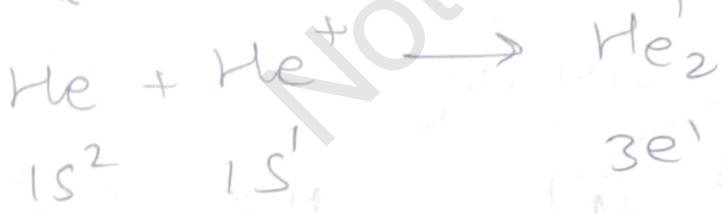


$$\text{MOC} = \sigma 1\text{s}^2 \sigma^* 1\text{s}^2$$

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

Hence it does not exist

③ He_2^+ ion



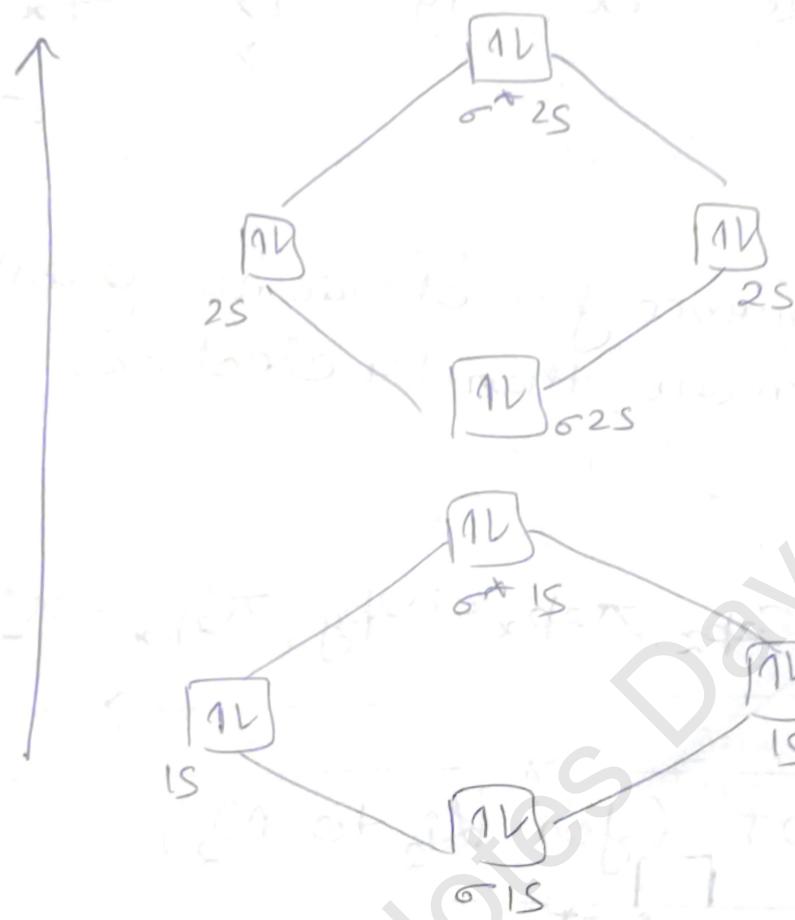
$$\text{B.O.} = \frac{2 - 1}{2} = \frac{1}{2} = 0.5$$

Paramagnetic bcoz of unpaired e^-

③ Be_2



$1S^2 2S^2$ $1S^2 2S^2$ $8e^-$

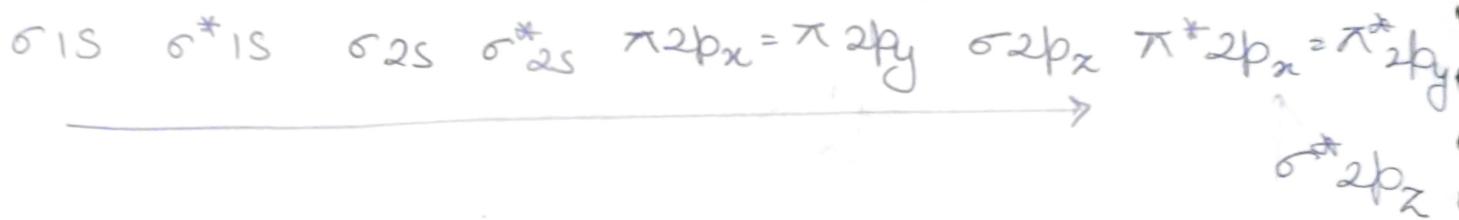


$$\text{B.O.} = \frac{4 - 4}{2} = 0$$

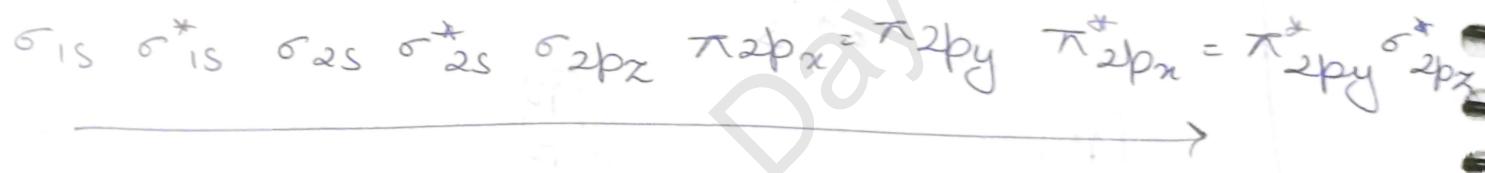
MOC = $\sigma 1S^2 \sigma^* 1S^2 \sigma 2S^2 \sigma^* 2S^2$

Diamagnetic box of absence of unpaired electrons

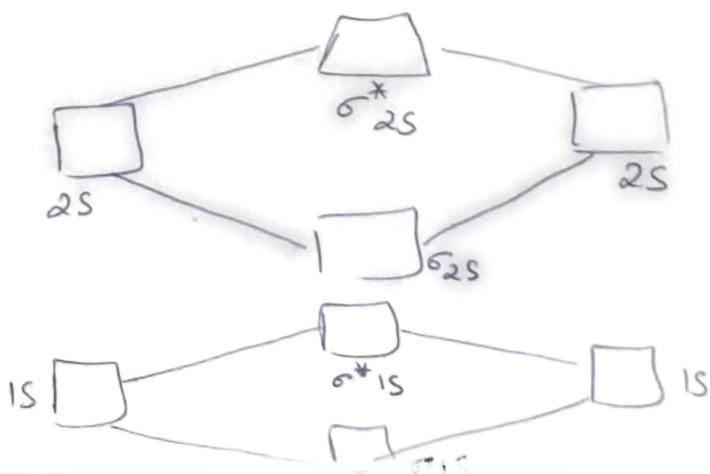
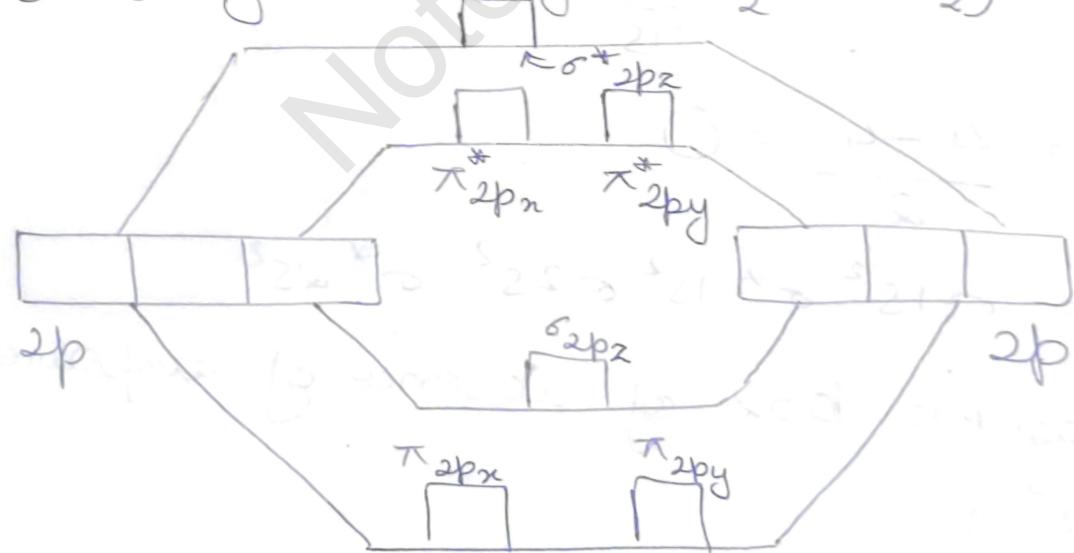
* Energy level sequence for atomic no. 7 upto 14 electron (Li, Be, B, C, N)



* Energy level sequence for atomic no. greater than 7 and more than 14 electrons (O₂ to F₂)



Structure of MOT (for Li₂ to N₂)

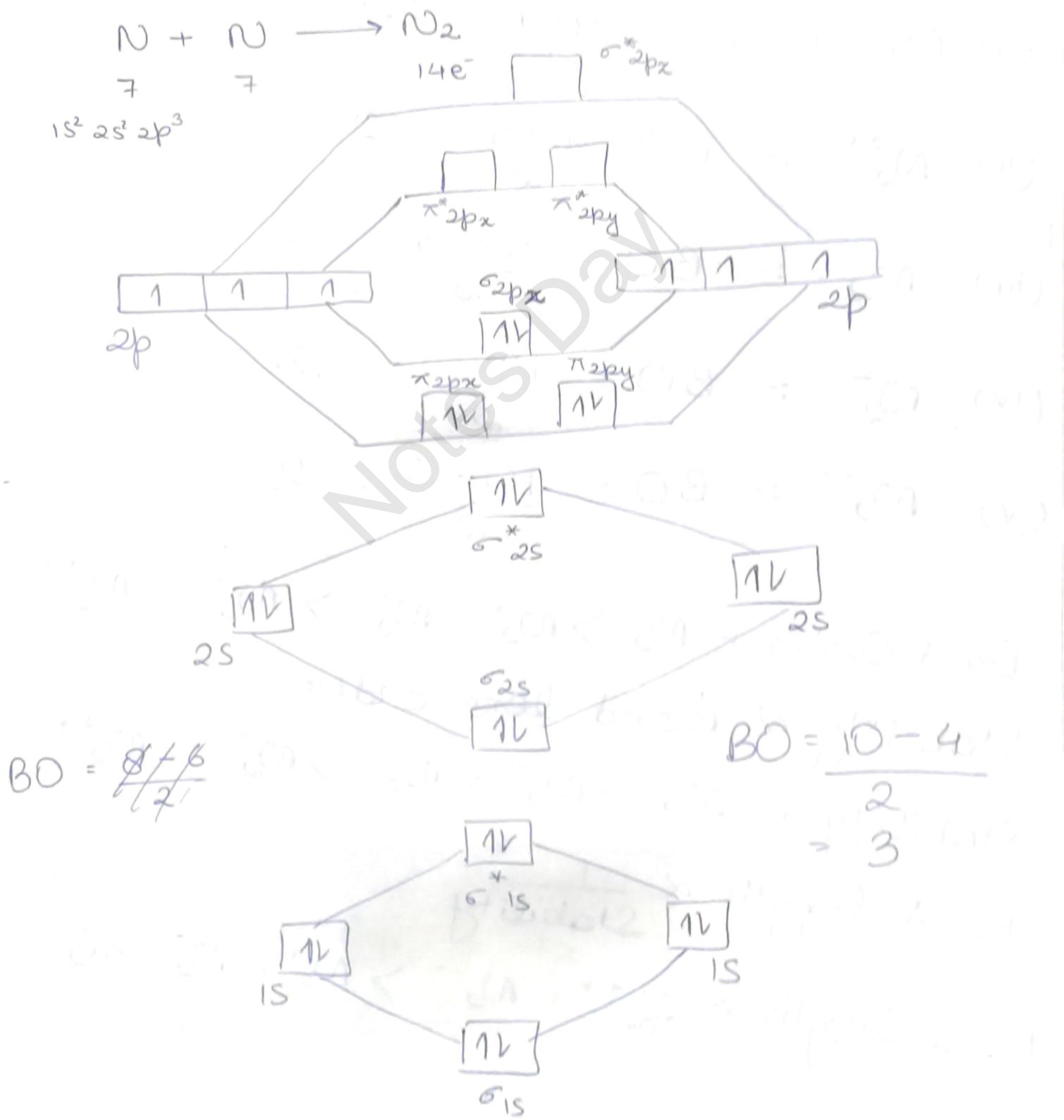


NOTE

Lithium to Nitrogen, the energies of $2s$ and $2p$ orbitals are quite close to each other because of repulsion between the electrons that occupy $2s$ and $2p$ orbitals.

The energy of σ_{2p} molecular orbital gets raised relatively to π_{2p} molecular orbitals.

Draw the molecular orbital diagram of N_2



i) N_2^+ (ii) N_2^{2+} (iii) N_2 (iv) N_2^- (v) N_2^{--}
 find stability acc. to B.O. or bond length

Stability \propto Bond Order

Stability $\propto \frac{1}{\text{Bond length}}$

$$(i) \text{N}_2^+ : \text{BO} = \frac{9-4}{2} = 2.5$$

$$(ii) \text{N}_2^{2+} : \text{BO} = \frac{8-4}{2} = 2$$

$$(iii) \text{N}_2 : \text{BO} = \frac{10-4}{2} = 3$$

$$(iv) \text{N}_2^- : \text{BO} = \frac{10-5}{2} = 2.5$$

$$(v) \text{N}_2^{--} : \text{BO} = \frac{10-6}{2} = 2$$

Bond Order : $\text{N}_2 > \text{N}_2^+ = \text{N}_2^- > \text{N}_2^{--} = \text{N}_2^{++}$

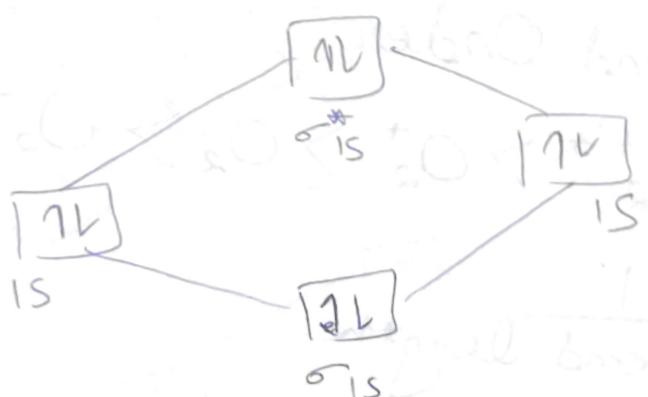
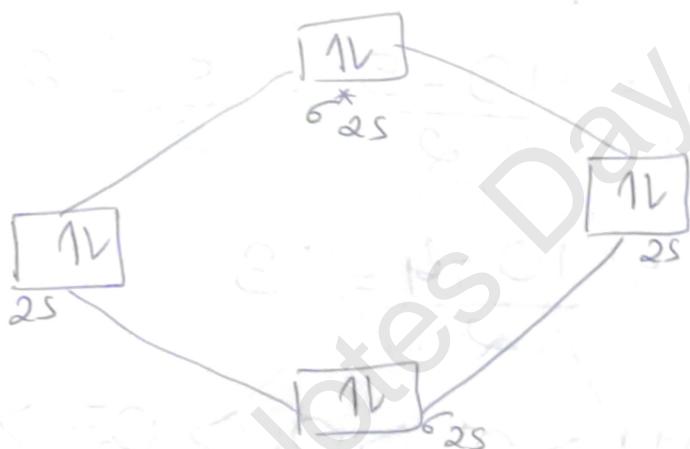
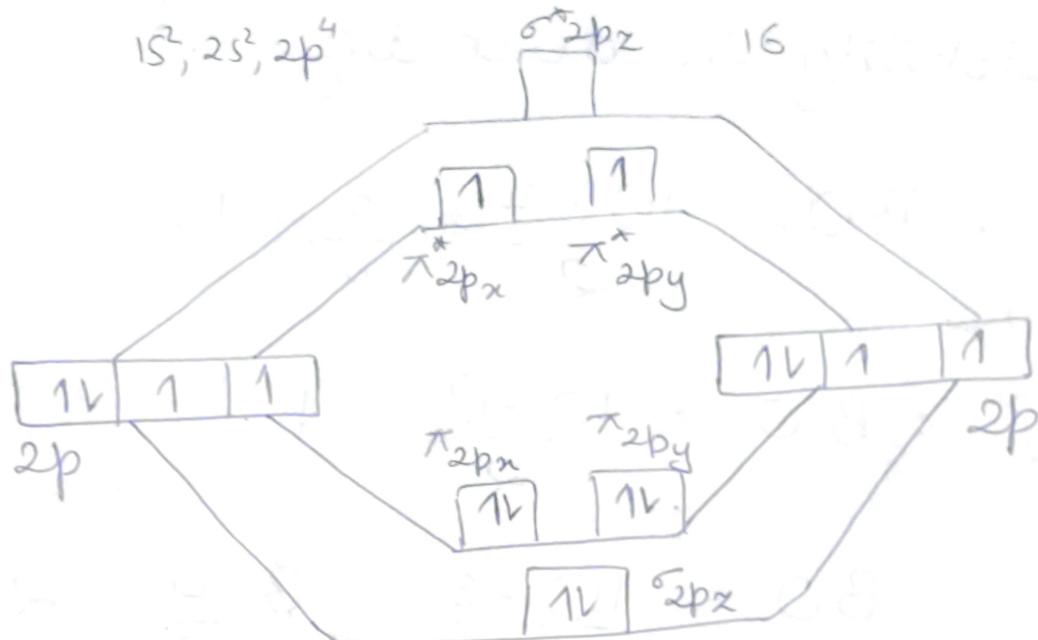
Stability \propto Bond ~~zero~~ order

Stability $\propto \text{N}_2 > \text{N}_2^+ = \text{N}_2^- > \text{N}_2^{--} = \text{N}_2^{++}$

Stability : $\text{N}_2 > \text{N}_2^+ = \text{N}_2^- > \text{N}_2^{--} = \text{N}_2^{++}$

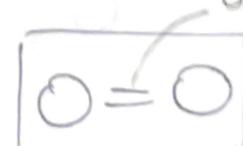
Bond length $\propto \frac{1}{\text{Stability}}$

Bond length $\Rightarrow \text{N}_2^{++} = \text{N}_2^{--} > \text{N}_2^+ = \text{N}_2^- > \text{N}_2$



MOC : $\sigma 1S^2, \sigma^{*} 1S^2, \sigma 2S^2, \sigma^{*} 2S^2, \sigma 2P_z^2, \pi^{*} 2P_x^2, \pi^{*} 2P_y^2$
 $\pi^{*} 2P_x^1, \pi^{*} 2P_y^1, \sigma^{*} 2P_z^0$

$$B.O. \Rightarrow \frac{10 - 6}{2} = \frac{4}{2} = 2$$



Paramagnetic bcoz of unpaired electrons



Find stability in descending order

(i) O_2^- : B.O. = $\frac{10-7}{2} = \frac{3}{2} = 1.5$

(ii) O_2^{--} : B.O. = $\frac{10-8}{2} = \frac{2}{2} = 1$

(iii) O_2 : B.O. = $\frac{10-6}{2} = \frac{4}{2} = 2$

(iv) O_2^+ : B.O. = $\frac{10-5}{2} = \frac{5}{2} = 2.5$

(v) O_2^{++} : B.O. = $\frac{10-6}{2} = 3$

Bond Order: $O_2^{++} > O_2^+ > O_2 > O_2^- > O_2^{--}$

Stability \propto Bond Order

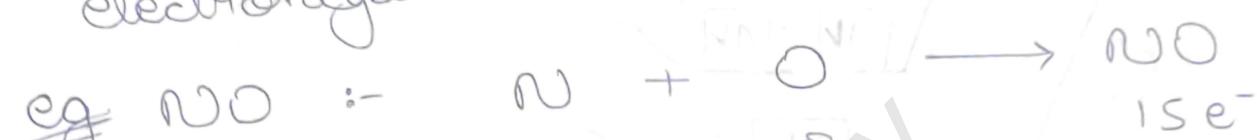
Stability = $O_2^{++} > O_2^+ > O_2 > O_2^- > O_2^{--}$

Stability $\propto \frac{1}{\text{Bond Length}}$

Bond length $\Rightarrow O_2^- > O_2^- > O_2 > O_2^+ > O_2^{++}$

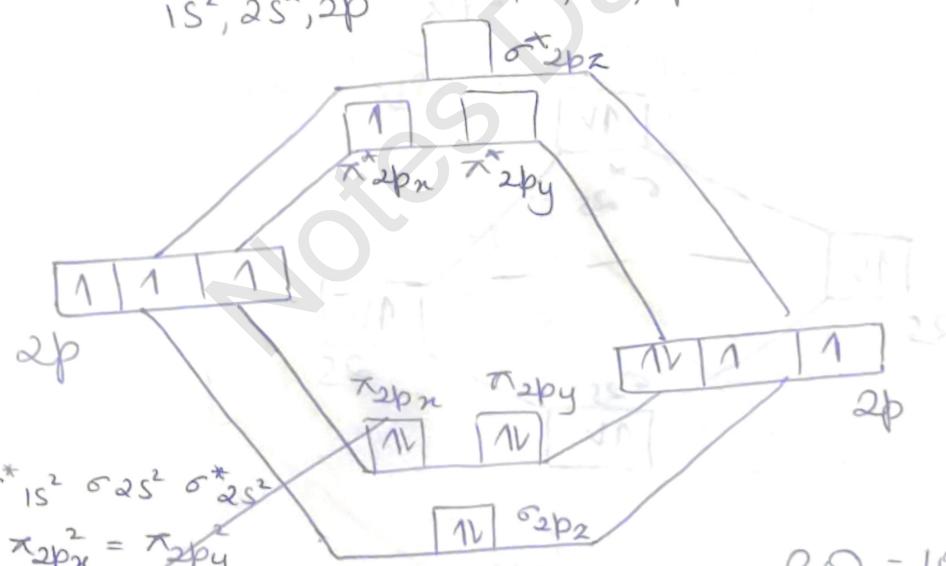
Heteronuclear diatomic Molecule

- A B type of molecule are known as hetero nuclear diatomic molecule
- The M.O. diagram of these differ from that of homo
- The M.O. diagram of these is not symmetrical
- The energy level of more electronegative is slightly lower than that of the less electronegative atom



N : 7
 $1s^2, 2s^2, 2p^3$

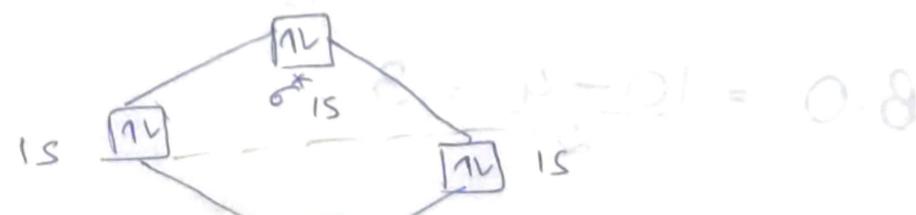
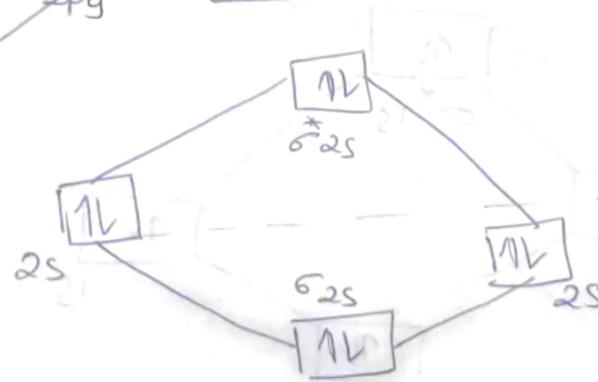
O : 8
 $1s^2, 2s^2, 2p^4$



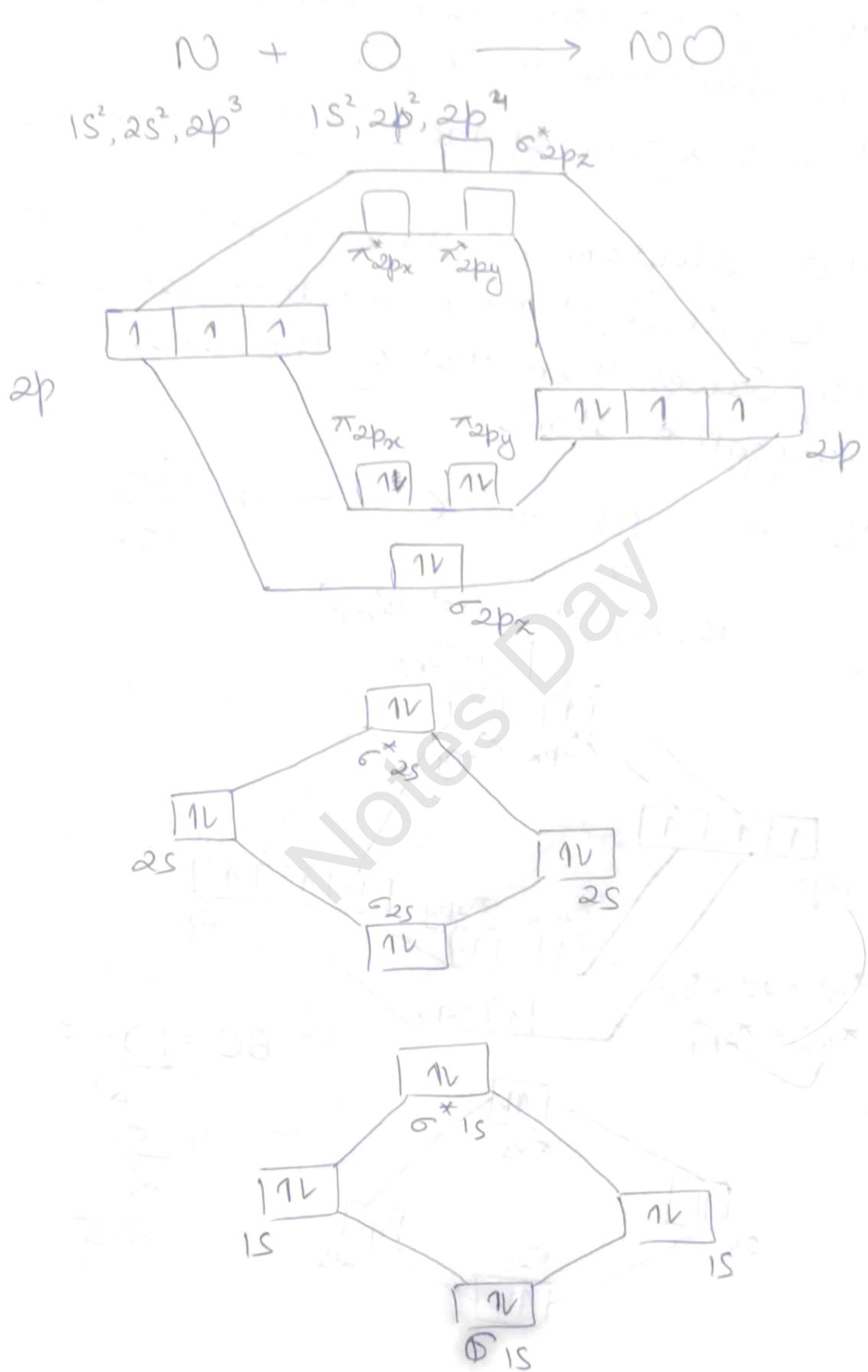
$$\text{MOC: } \sigma_{1s}^2 \sigma^*_{1s}^2 \sigma_{2s}^2 \sigma^*_{2s}^2 \sigma_{2p_z}^2 \sigma^*_{2p_z}^2 = \pi_{2p_y}^2 \pi^*_{2p_x}^2$$

$$BO = \frac{10 - 5}{2}$$

$$= \frac{5}{2} = 2.5$$



~~Imp~~ NO⁺



$$B.O. = \frac{10 - 4}{2} = 3$$

Ques. Justify the bond length of CO^+ is 1.115 \AA
and CO is 1.128 \AA .



$1s^2, 2s^2, 2p^2$ $1s^2, 2s^2, 2p^4$



For CO ,

M.O.C :

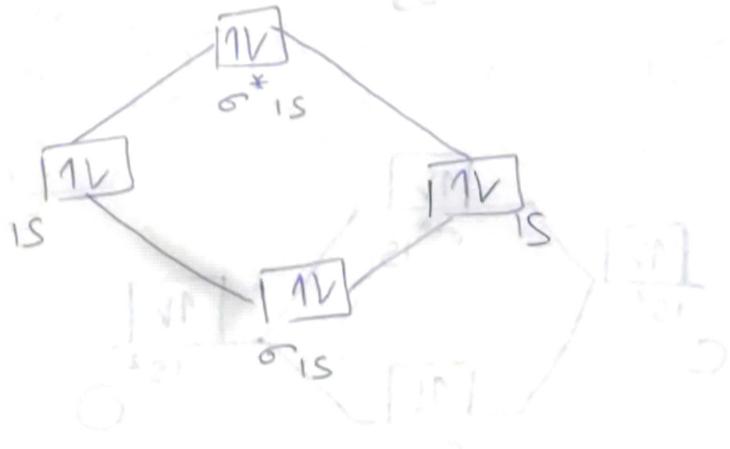


$$\pi_{2p_x}^2 = \pi_{2p_y}^2$$

$$\text{B.O.} = \frac{10 - 4}{2} = 3$$

For CO^+ ,

$$\begin{aligned} \text{B.O.} &= \frac{9 - 4}{2} \\ &= 5/2 \\ &= 2.5 \end{aligned}$$



for CO

$$\text{B.O.} = 3$$

$$\text{Bond length} = 1.128 \text{ \AA}$$

for CO^+

$$\text{B.O.} = 2.5$$

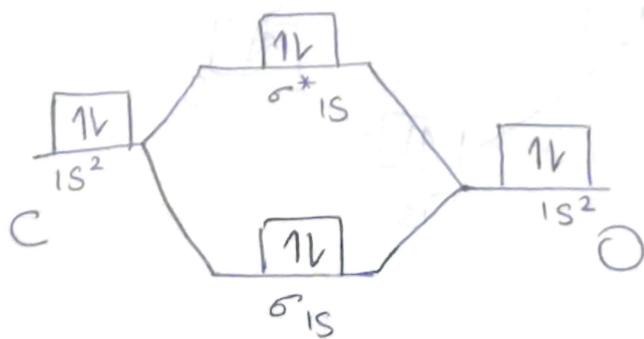
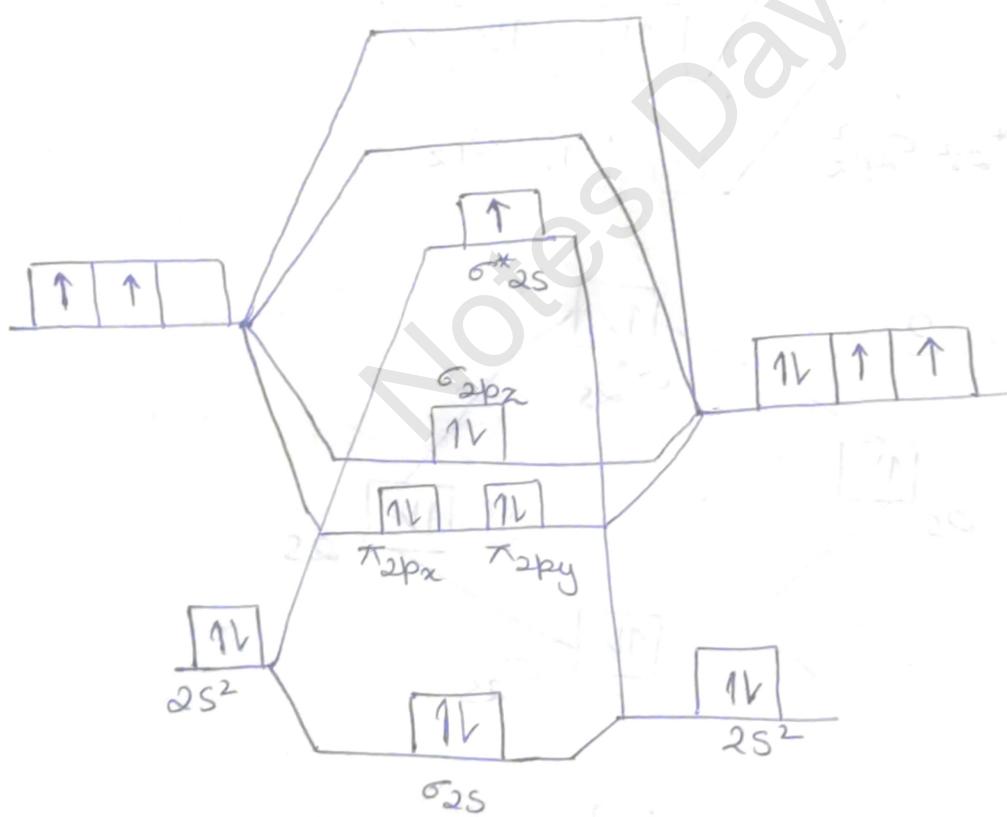
$$\text{Bond length} = 1.115 \text{ \AA}$$

Now, as we know that Bond length $\propto \frac{1}{\text{Bond order}}$

hence it is a rule out.

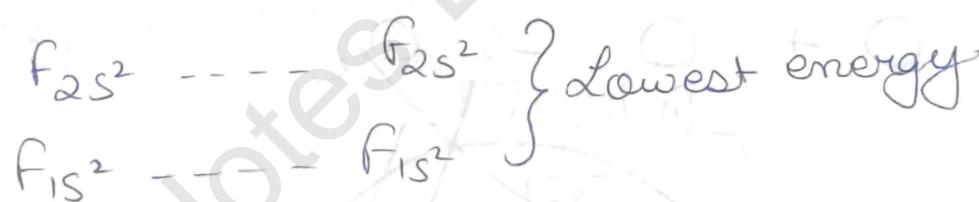
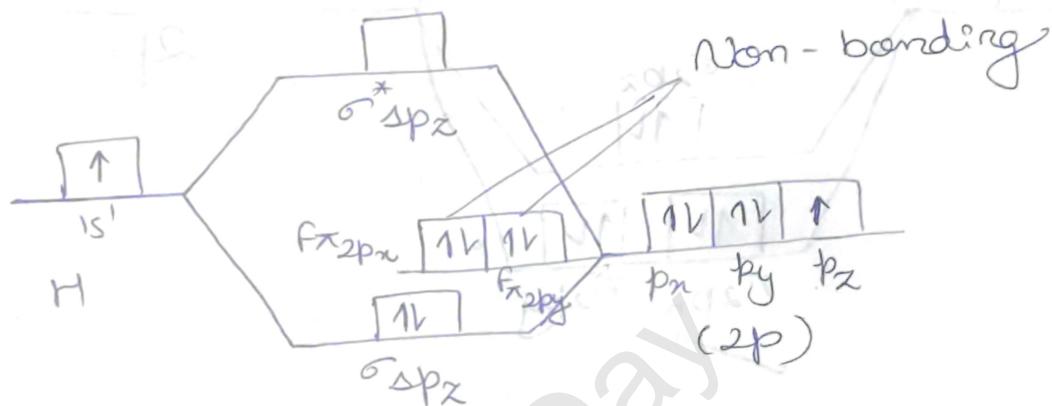
Therefore, for CO^+ \rightarrow

Experimentally, it is found that the bond length in CO to CO^+ indicates the electron must have been removed from the σ_{2s}^* orbital.



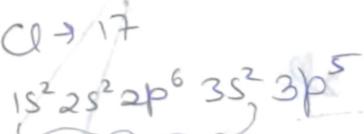
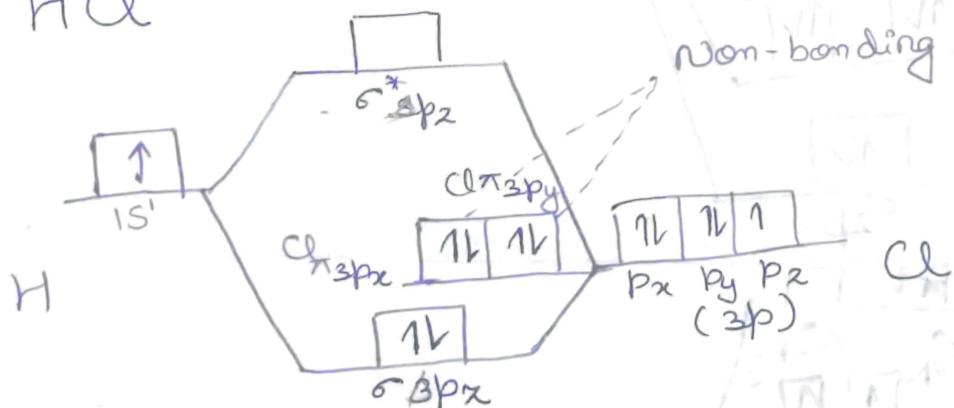
$\Rightarrow HF$

- * $1s'$ of hydrogen will not combine with $1s^2, 2s^2$ of fluorine because of higher energy gap of fluorine
- * $1s'$ of hydrogen will not combine with fluorine $2p_x$ and $2p_y$ of fluorine because of symmetry consideration.
- * $1s'$ of hydrogen will combine with $2p_z$ of fluorine



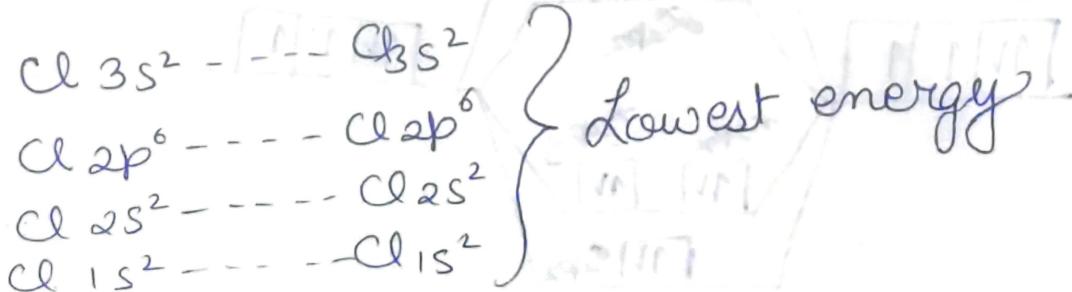
$$B.O. = \frac{2 - 0}{2} = 1$$

$\Rightarrow HCl$



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

diamagnetic

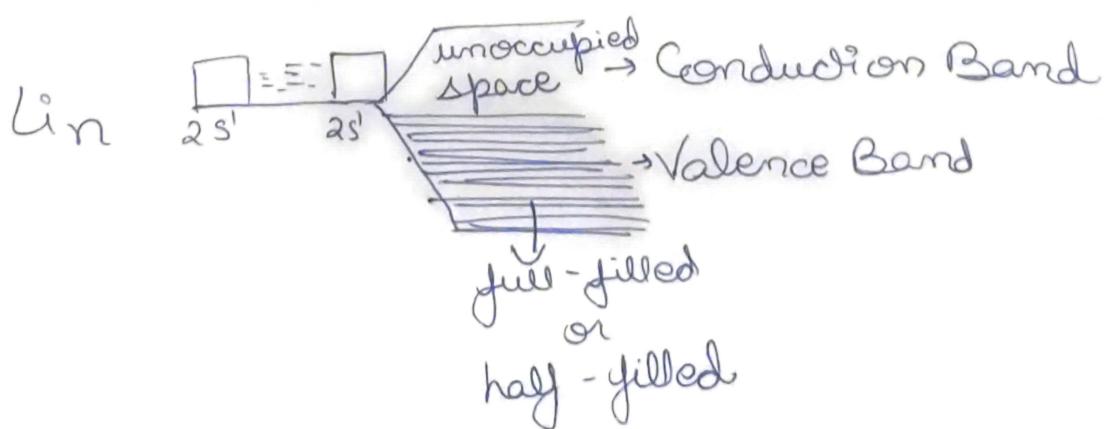
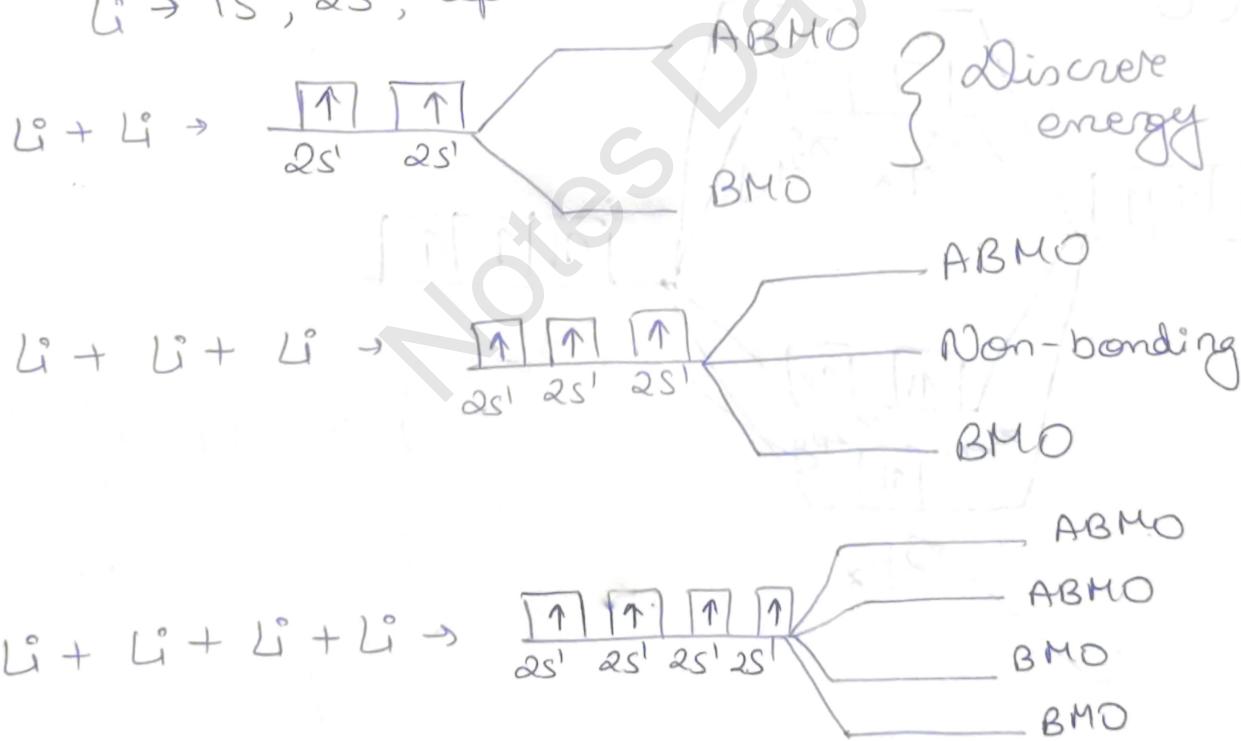


Bond Theory Of Metallic Solid

This theory is extended in solid referred to as band theory of metallic solid. This theory is explained on the basis of molecular orbital theory.

Acc. to this, a metal lattice contains a large no. of metal atom. The atomic orbital of atom combine and give same no. of molecular orbitals.

e.g. Li and Na

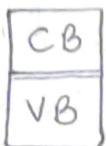


There are 3 types of band

Energy band → It is the region where the probability of finding the electron is maximum.

Forbidden zone → It is the region where the probability of finding the electron is zero.

① Conductor → There is no energy gap or the bands are overlapping, then such materials are called conductors. eg: metals



② Semi-conductor



→ These are of two types - Intrinsic and Extrinsic.

Intrinsic

- pure semiconductors
- small energy gap
- sufficient to promote e^- from VB to CB
- conductivity \uparrow se with rise in temp

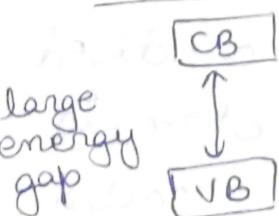
p-type

• doped with grp(III) impurity

n-type

• doped with grp(V) impurity

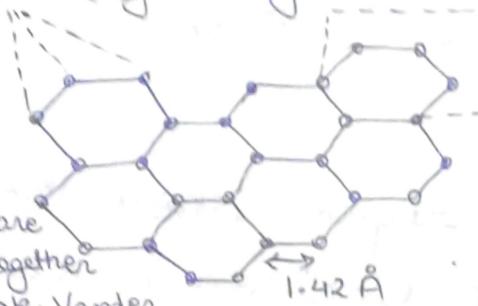
③ Insulator



→ There is a large band gap, hence e^- cannot be promoted from valence band to conduction band where they could move freely.

Write a short note on Graphite

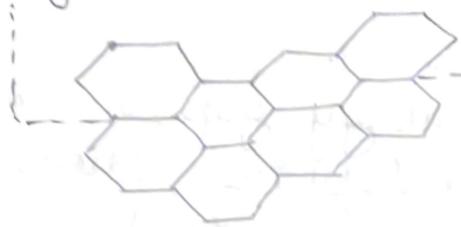
carbon atom forming
a network of hexagon



layers are held together by weak Vander Wall's force

each carbon atom linked by only three other carbon atom by covalent bond

3.41 Å



- * In graphite, each carbon is sp^2 hybridized and is linked to three other carbon atom by covalent bond.
- * The bonding b/w atom within a layer is strong covalent. Several such layers are held together by weak Vander Wall's force. Therefore, graphite is composed of 2-D, flat, layer structure.
- * C - C distance within a layer is 1.42 Å and layer distance is 3.41 Å. Consequently, even a small force is sufficient to slide the layer parallel to each other bcoz of weak Vander Wall's force. It has low coefficient friction.
- * Graphite is very soapy to touch, soft and non-inflammable. It is used as a lubricant upto 370°C . Above the temp. it is oxidised
- * The fourth valency electron of each C-atom is free, which can move easily from one carbon to another under the applied potential. Therefore, it is a good conductor of electricity.

Write a short note on Fullerenes

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* Introduction

- It was discovered by H W Kroto and R Smalley at Rice University, USA in 1985.
- Popularly known as Buckminsterfullerene in honour of Arch. Buckminster Fuller, who designed geodesic structure based on pentagons & hexagons.

* Preparation

- 1 Vaporizing a graphite rod in helium atmosphere
- 2 Mixture of C_{60} , C_{70} , etc are formed which are separated by solvent extraction
- 3 Pure C_{60} is isolated from this mixture by column chromatography

* Structure (bucky ball)

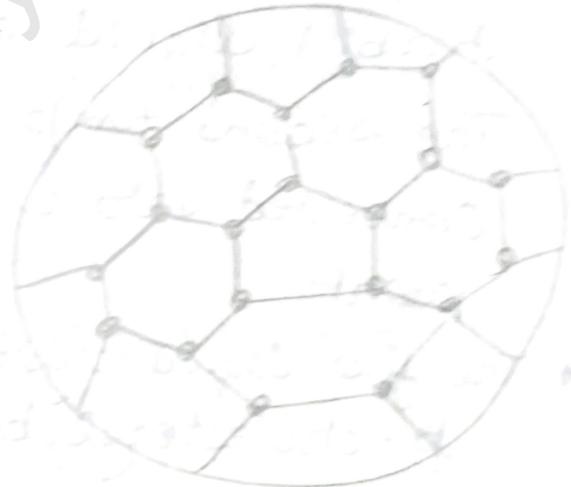
- Truncated icosahedron
- A polygon with 60 vertices, 32 faces, 12 are pentagon and 20 hexagon
- The molecule is aromatic and has several resonance structures.
- C_{60} forms a normal face centered cubic lattice

* Properties

- sp^2 hybridized
- Black powdery material, forms deep magenta solution when dissolved in benzene
- Very tough, thermally stable (it can be sublimed at $600^\circ C$ under vacuum)
- Exists as discrete molecule, can be compressed to lose 30% of volume without destroying structure

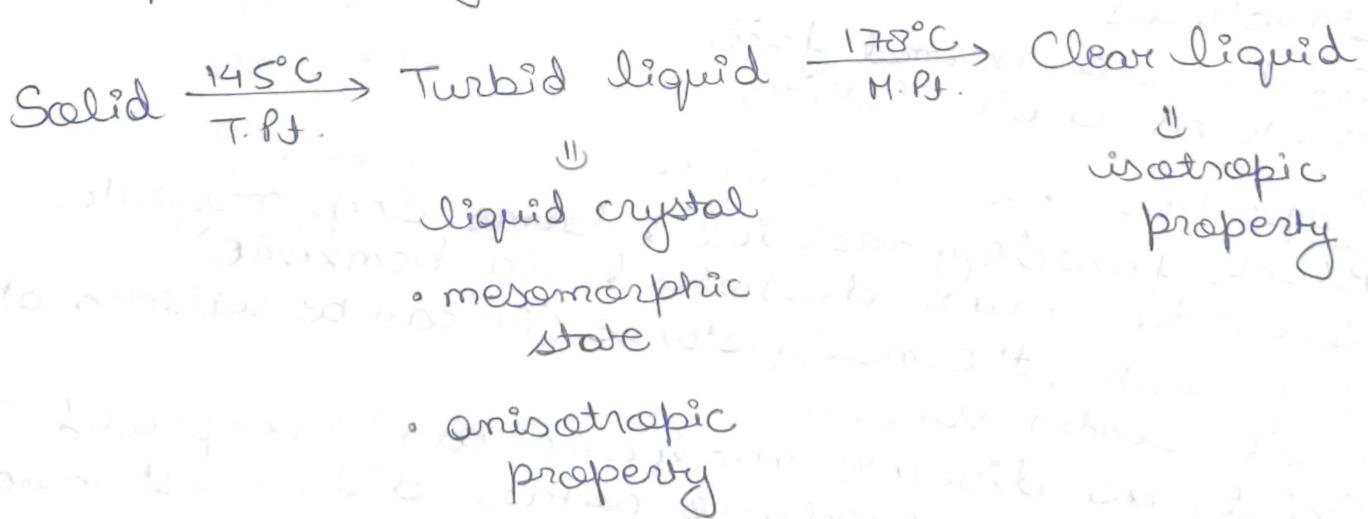
* Uses

- as lubricant, as superconductor when mixed with alkali metals, used as soft ferrimagnet, in non-linear optical devices, etc



Liquid Crystals (10 marks)

- * A state of matter, i.e. intermediate between solid crystalline and ordinary liquid is called as liquid crystal. It is also known as mesomorphic state.
- * All solids do not change sharply from orderly solids to disorganized liquid when they melt.
- * Certain solids which when heated undergo two sharp phase transformations. The first temp. at which solid is converted into turbid liquid called as transition point. The second temp. at which turbid liquid is converted into clear liquid is called melting point.
- * The first liquid crystal was discovered in 1888 by p -cholesteryl benzoate ($C_6H_5COOC_{27}H_{45}$)



Structure: $X - \text{C}_6\text{H}_4 - \text{C}_6\text{H}_4 - X$

Classification

Based on molecular ordering and temperature

① Thermotropic

↓
change in temp.
results to change
in state

- ↓
(i) Smectic Lcs
- (ii) Nematic Lcs
- (iii) Cholesteric Lcs
- (iv) discotic Lcs

② Lyotropic

↓
change in solvent conc.
results to change in
meso phase

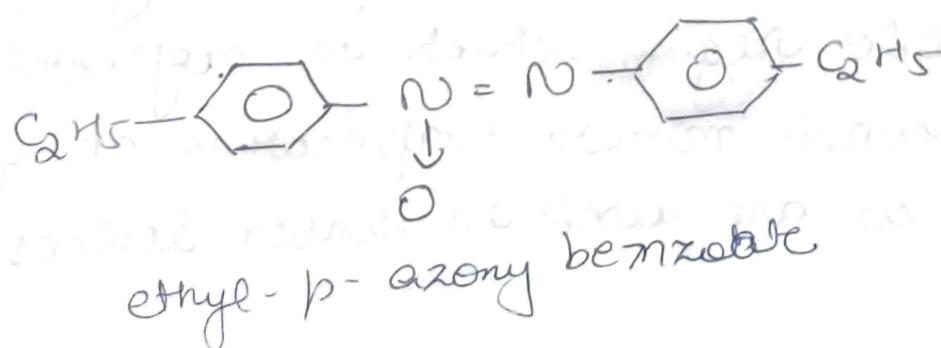
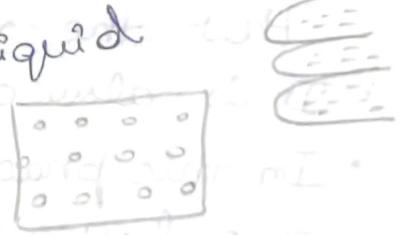
- ↓
layer
(i) (Lamellar) phase
- (ii) Hexagonal phase
- (iii) Cubic phase

* Thermotropic Liquid Crystal

Class of compound which exhibits liquid crystalline phases as the temperature is changed

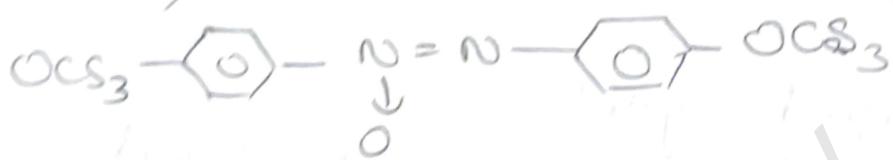
(i) Smectic Lcs

- When view in polarized light, they show soap like structure
- They do not flow as normal liquid
- They flow in layers
- They have limited mobility
- They have orientation as well
- They show positional orders.
- eg: ethyl-p-azoxy benzoate
- eg: ethyl-p-azoxy cinamate



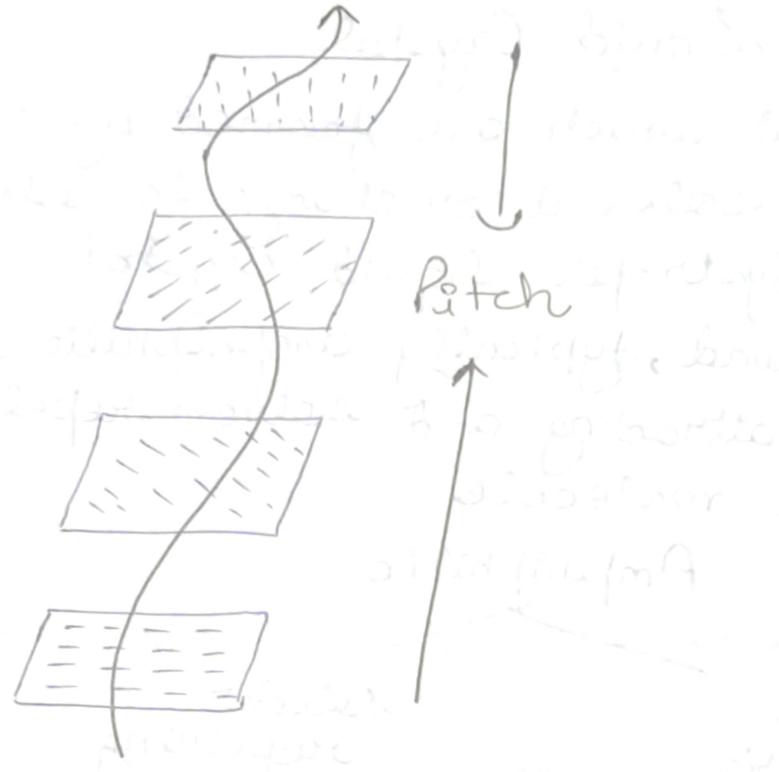
(ii) Nematic Lcs

- In polarized light they show thread like structure
- They show orientational order but show total loss of positional order
- They flow as normal liquid
- They are free to move
- e.g., p-oxy anisole
p-oxy phenetole



(iii) Cholesterics Lcs (Chiral Nematic Lcs)

- These are formed in optically active compound
- The name of this Lc is derived from cholesterol
- The necessary condⁿ for this Lc formation is that the molecule should be chiral
- It is also called chiral nematic liquid crystal
- In this phase, molecule twist slightly from one layer to next resulting in spiral formation
- It is characterised by an important property i.e. pitch which is defined as the distance over which a complete rotation of 360° is completed. Pitch determine the wavelength of light in visible region which is reflected.
- This L.c can sense minute temperature change i.e. 0.001°C so are used in sensor devices.



(iv) Discotic LC

- Molecules having disc-like or plate-like structure
- Discotic LC is further sub-divided into :
 1. Nematic Discotic LC
 2. Smectic Discotic LC (Columnar Discotic LC)
- In Nematic Discotic LC, molecule show orientational order but total loss of positional order but
- Molecules are arranged randomly and free to move



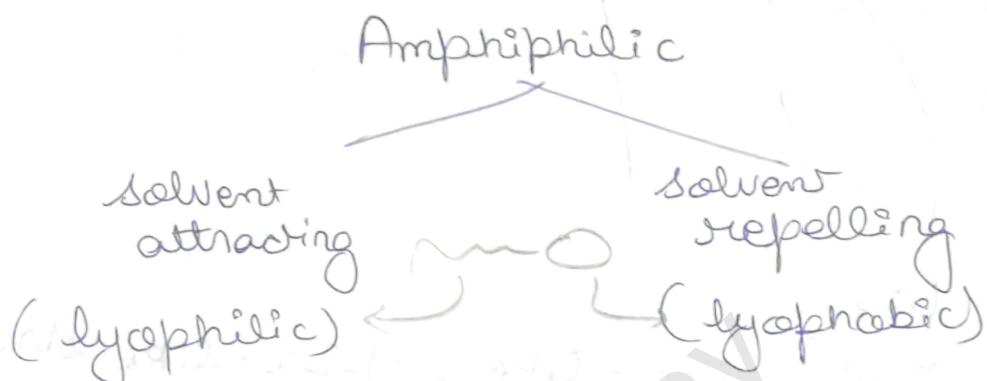
Smectic Discotic LC

Most of the molecules in this phase have both orientational and positional order. Molecules are arranged in columns and Columns are arranged in hexagonal manner.



* Lytotropic Liquid Crystal

- Liquid crystal which are formed by change in concⁿ of solvent, or change in solvent are called lyotropic liquid crystal
- Such compound, typically amphiphilic molecule i.e. solvent attracting and solvent repelling in the same molecule



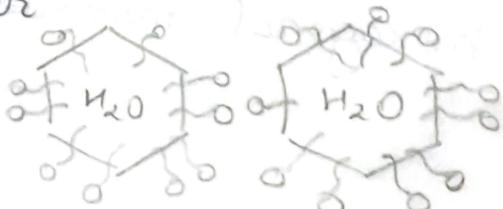
(i) Demellar Phase

- These phases are characterised by well defined thickness made by amphiphilic molecule but no order within the layer.
- The bi-layer are separated by H₂O solvent



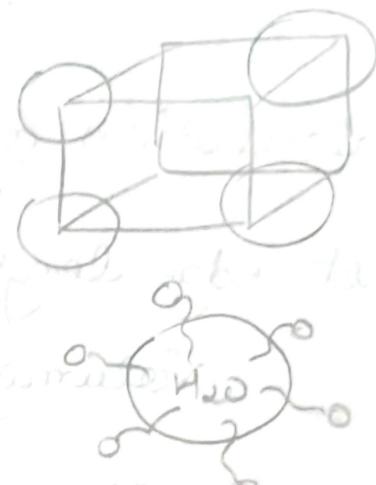
(ii) Hexagonal Phase

- In such phases amphiphilic molecule form cylindrical structure with polar head forming outer shell and water within the layer



(iii) Cubic Phase

- In such phases, amphiphilic molecule pack into the sphere.
- The space b/w the sphere is taken up by the water as solvent.



* Applications

- Liquid crystal used in colour sensor, temp. sensor
- used in display devices; eg laser lighting blackboard
- Cholesteric LC is used to detect tumor in the body. This method is known as thermography

→ Solid definition

$$\text{mol/g} = M \times \frac{1}{Z} = 6$$

→ Type

→ space lattice - ~~lattice~~ arrangement of atoms

→ lattice point - primitive - Only at edges (SCC)

→ unit cell - non-primitive edge + other part (fcc/bcc/ccc)

building of 316 - 2nd part

→ calculation of no. of atom / unit cell p.e.o. = 8

$$SCC = 1$$

$$bcc = 8/1+1+2$$

$$fcc = 8/1+\frac{6}{2} = 4 \times 8 = 32 \times 0.15 \times 0.18 \times 0.18$$

$$= 5.04 \times 0.1 \times 0.18 \times 0.18 \times 0.18 \times 8.01 = \frac{M}{P}$$

Solids

* Calculation of density of unit cell

Let edge length of unit cell = a cm

Volume of unit cell = a^3 cm³

$$\text{Density} = \frac{\text{mass}}{\text{Volume}}$$

mass = no. of atom / unit cell * mass of each atom

$$\text{mass} = Z \times m$$

$$\text{Mass of each atom} = \frac{\text{atomic wt.}}{\text{Avagadro No.}} \times \left(\frac{M}{A_D} \right)$$

$$d = \frac{Z \times M}{a^3 \times N_A} \text{ gm/cm}^3$$

if edge length is expressed in picometer, then

$$1 \text{ pm} = 10^{-12} \text{ m} = 10^{-10} \text{ cm}$$

Ques. A fcc structure of an element has $\rho = 10.3 \text{ g/cm}^3$ and has $a = 310 \text{ pm}$. Calculate the atomic mass of element

$$10.3 = \frac{4 \times M}{(310 \times 310 \times 310 \times 10^{-30} \times 6.022 \times 10^{23})}$$

$$M = \frac{10.3 \times 310 \times 310 \times 310 \times 10^{-7} \times 6.022}{4}$$

$$M = 46.2 \text{ gm}$$

Ques. Calculate the no. of atom/unit cell of a metal having lattice parameter 2.9 Å and density 7.8 g/cc, atomic wt. of metal is 55.85.

$$d = \frac{Z \times M}{a^3 \times N_A}$$

$$7.8 = \frac{Z \times 55.85}{2.9 \times 2.9 \times 2.9 \times 10^{-24} \times 6.022 \times 10^{23}}$$

$$Z = \frac{7.8 \times 2.9 \times 2.9 \times 2.9 \times 6.022 \times 10^{-23}}{55.85}$$

$$Z = 2$$

(Hence, bcc lattice)

Ques. A metal (at. mass = 50) has a bcc crystal. Density of which is 5.96 g/cc. Find out the volume.

$$d = \frac{Z \times M}{a^3 \times N_A}$$

$$5.96 = \frac{2 \times 50}{a^3 \times 6.022 \times 10^{-23}}$$

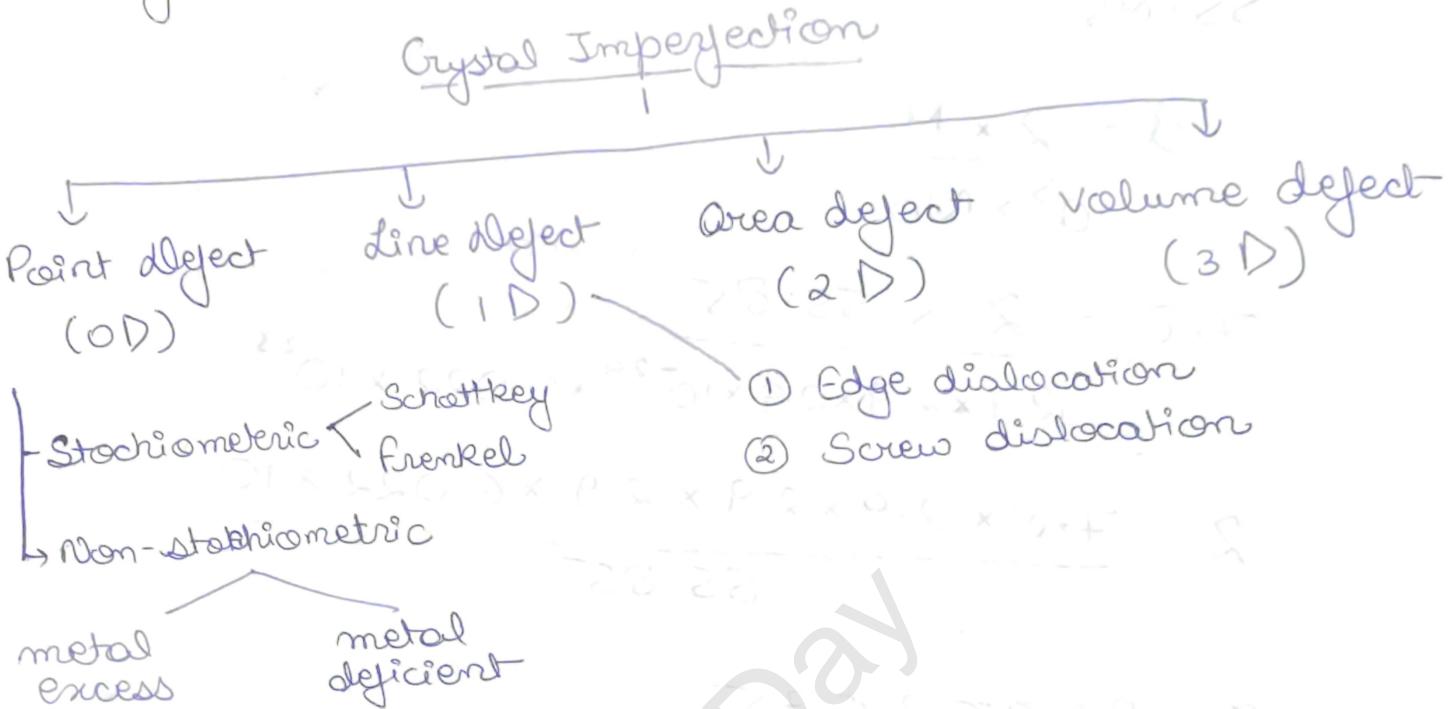
$$a^3 = \frac{2 \times 50}{5.96 \times 6.022 \times 10^{-23}}$$

$$a^3 = \frac{100 \times 10^{-23}}{5.96 \times 6.022}$$

$$= 0.0278 \times 10^{-21}$$

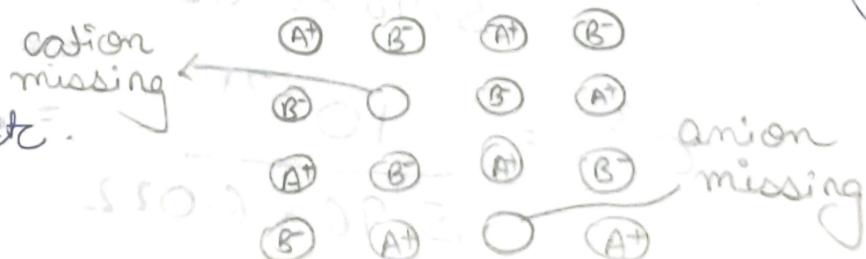
$$a^3 = \frac{10^{-21}}{5.96 \times 6.022} = 2.78 \times 10^{-23} \text{ cm}^3$$

* Crystal Imperfection
Any deviation from ordered arrangement in a crystal.



* Stoichiometric Defect

- A point defect in which the no. of cation and the no. of anion are equal even after imperfection in order to maintain stoichiometry.
- It is further sub-divided into :-
1. Schottky defect :- It arises when a pair of cation and anion are missing from their respective lattice site. The unoccupied points are called holes. Because of pair, electrical neutrality is maintained but density decreases. It occurs in high coordination no. ionic compounds where cation & anion are of similar size.
eg. CsCl , NaCl , etc.



2. Frenkel defect: Either cation or anion is missing from displaced from lattice site to interstitial position leaving a hole. Electrical neutrality and density are maintained as before. This defect is observed in low-coordination no. compounds. e.g. AgCl, AgBr.



* Non-stoichiometric

* Non-stoichiometric: These point defect in which the ratio of cation and anion is not equal. It is further divided into

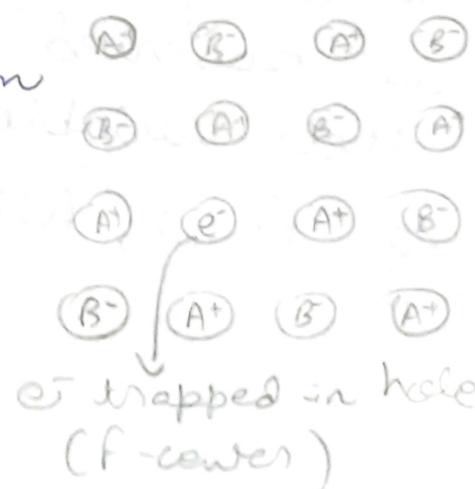
1. Metal excess defect

- (a) Due to anion vacancy
 - (b) Due to interstitial cation
- * In these defect, metals are in excess and may arise by 2 methods.

(i) Due to anion vacancy:

An anion may be absent from the lattice site leaving a hole which is occupied by e^- , i.e., f-center (Farr \rightarrow colour)

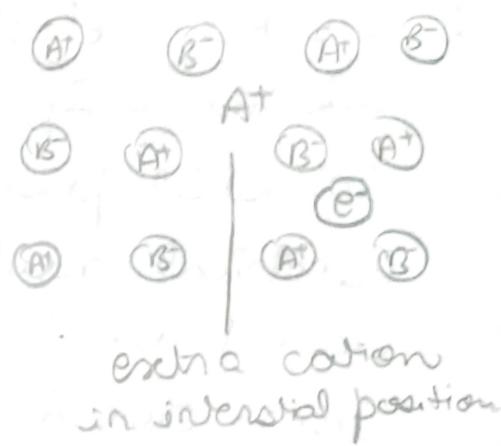
e.g. LiCl, NaCl, KCl
↓ ↓ ↓
pink yellow violet



Due to interstitial cation

An extra cation occupy an interstitial position. Electrical neutrality is due to the presence of e^- in interstitial position

eg ZnO , CdO



ZnO is white when cold but yellow when hot. On heating, some of oxide ions (O^{2-}) escape as O_2 , leaving behind excess of Zn^{2+} & e^- in the lattice leading to excess metal ions and deficiency of oxide ions. The colour arises due to the movement of e^- cation.

* Metal deficiency defect

→ Due to cation vacancy

A +ve ion / cation is absent from the lattice site leaving a hole and charge is balanced by adjacent cation having 2 charges instead of 1. This type of defect is observed in transition metals due to their variable oxidation states.

eg FeO , NiO

Due to interstitial anion

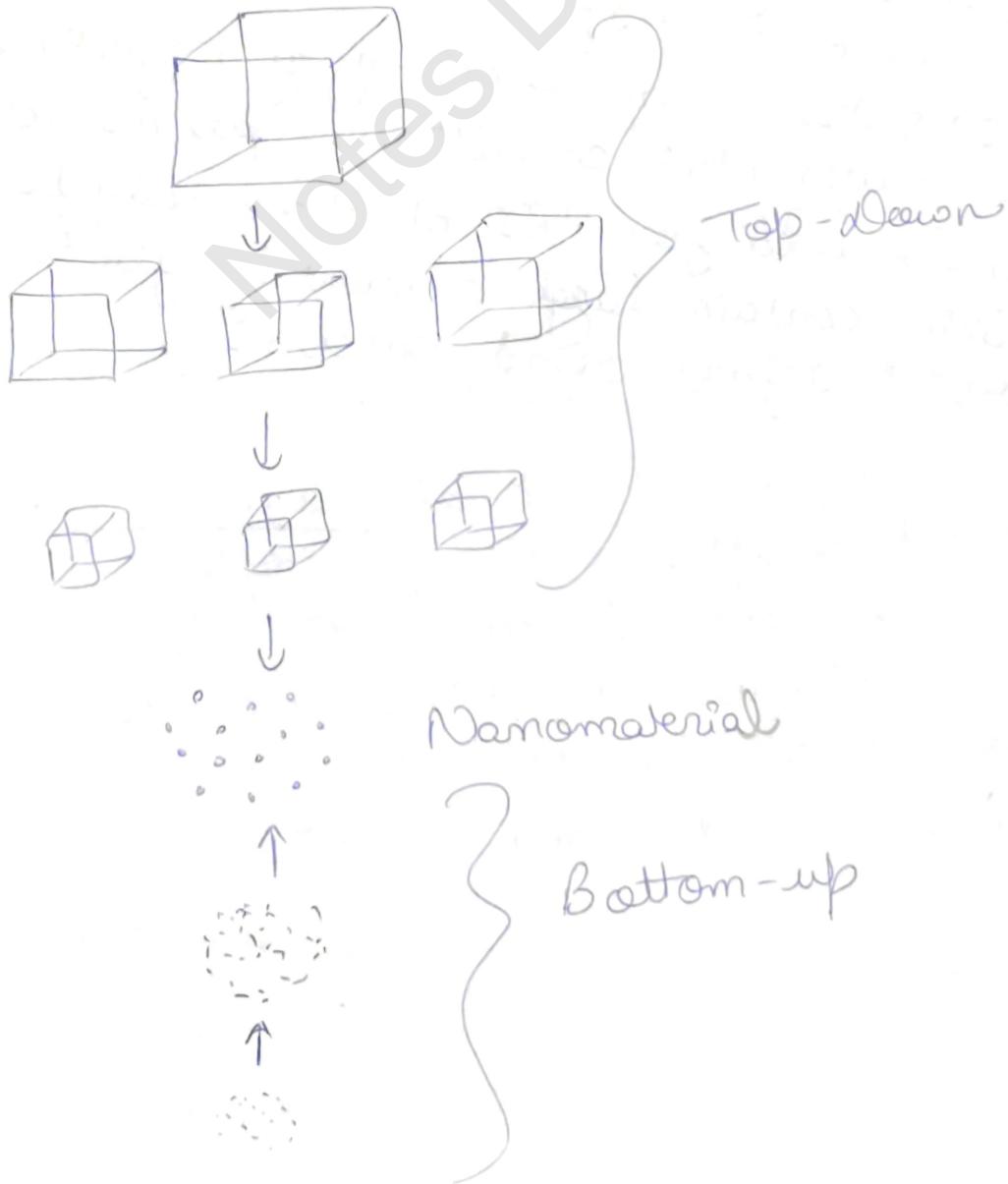
Due to large size of anion, it will be difficult for them to fit.

Nanomaterials and Nanotechnology

Nanomaterials which have structural constituents, one dimension less than 100 nanometers, are called as nanomaterials.

Methods of preparation

- ① Top-down Approach (Physical process)
- ② Bottom-up Approach (Chemical process)



Applications

- ① Nano crystalline zirconia (i.e. zirconium oxide)
It is hard and resistant ceramic which is chemically stable and bio-compatable
- ② It is used in the field of orthopedic and dental surgery
- ③ ~~exp~~ Carbon Nano Tubes (CNT) are used for flat panel display devices, eg:- LED, computer monitor
- ④ Transparent nano-particles of ZnO absorb UV light and are used in highly effective sunscreens.
- ⑤ Super Paramagnetic Iron Oxide Nanoparticles (SPIONS)
are used in MRI.
SPIONS have core consisting of magnetite (Fe_3O_4) and outer shell consisting of ~~pos~~ magnetite (Fe_2O_3).
They are used for MRI of those body parts which contain large amount of fluids such as internal injuries and cancerous