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~~Valence Bond~~

VALENCE BOND THEORY

- Pauling and Slater

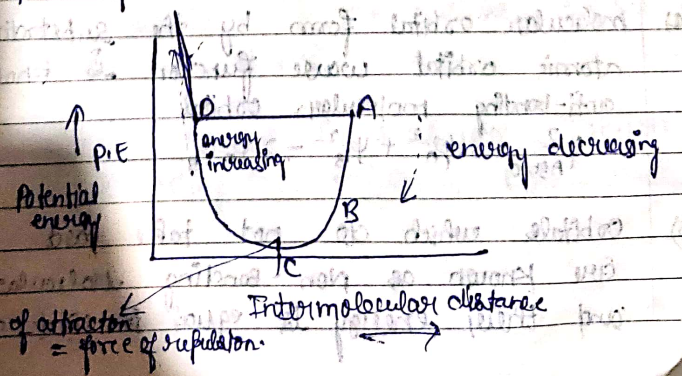
(i) This theory was proposed by Pauling and Slater. They explain the formation of covalent bond between two atoms by using the concept of electrostatic force.

→ This theory was failed due to some limitations.

LIMITATION OF V.B.T

(a) This theory does not explaining

(1) Paramagnetic nature of oxygen molecule
(2) Formation and structure of several compounds involving the concept of resonance and hybridisation
(3) This theory does not provide any explanation about the colour of the compounds
(4) This theory fails to explain the bonding in electron deficient compounds.



LCAO ... Atomic Orbitals.

MOLECULAR ORBITAL THEORY

→ This theory was proposed by Hund and Mullikan in 1932.

→ This theory was based on LCAO principle.

→ According to this theory :—

(1) Atomic orbitals of combining atoms having comparable energy and same symmetry, combine to form molecular orbitals. If ψ_A and ψ_B are the wave function of atom A and B then according to LCAO, $\boxed{\psi_{M.O} = \psi_A \pm \psi_B}$

(2) Number of molecular orbitals form is equal to the Number of overlapping atomic orbitals.

(3) Molecular orbital form by the addition of two atomic orbital wave function is known as Bonding Molecular orbital $\psi_{M.O} = \psi_A + \psi_B$ (Constructive interaction)
The probability of finding an electron in bonding molecular orbital will be
$\psi^2 = \psi_A^2 + \psi_B^2 + 2\psi_A\psi_B$

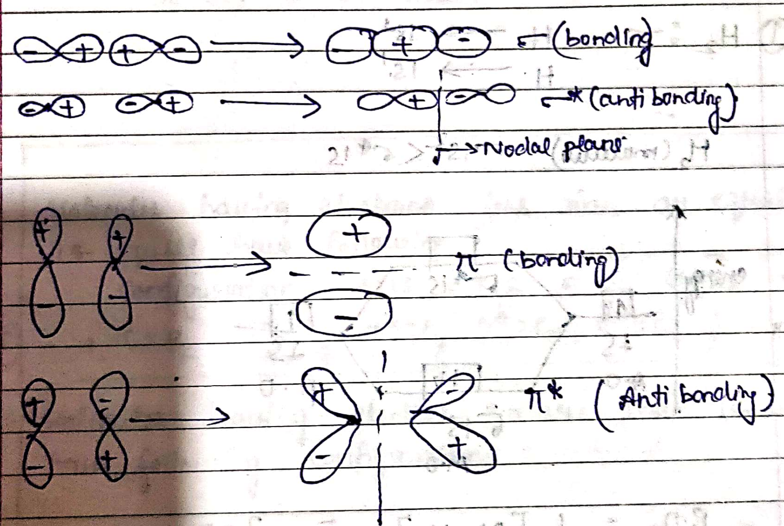
(4) molecular orbital form by the substraction of two atomic orbital wave function is known as anti-bonding molecular orbital
$\psi^2_{ABMO} = \psi_A^2 + \psi_B^2 - 2\psi_A\psi_B$

(5) Orbitals which do not take part in Bonding are known as Non-Bonding Molecular Orbital and their energy is equal to that of atomic

orbital.

(6) A Bonding molecular orbital has lower energy and higher stability than the Anti-Bonding Molecular orbitals.

(7) The shape of molecular orbital formed depends on the type of combining atomic orbitals. for example



(8) Atomic orbits are monocentric (movement of electron influenced by one nucleus) while M.O are polycentric in nature.

(9) Filling of Electrons in Molecular Orbitals takes place according to Aufbau, Pauli and Hund's Rule :-

$2p^3$ $2p^4$

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(10) Molecules having one or more unpaired electrons in their M.O. are paramagnetic while those with paired with electrons are diamagnetic in nature. (2)

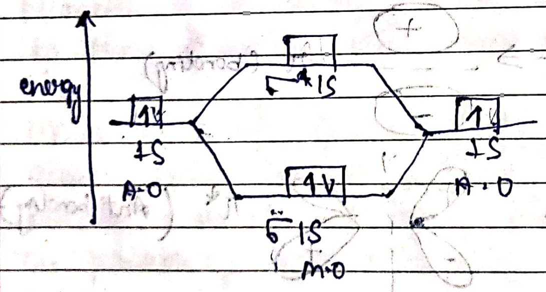
MOLECULAR ORBITAL DIAGRAM

It is a potential energy diagram which represents combining of atomic orbitals and formation of molecular orbits.

(1) H_2 : H $\longrightarrow 1s^1$

H $\longrightarrow 1s^1$

H_2 (molecule) $\sigma 1s^2 < \sigma^* 1s$



$$B.O = \frac{1}{2}[N_b - N_a] = \frac{2-0}{2} = 1$$

Since all electrons are paired in M.O, so H_2 is diamagnetic in nature.

H → 1s

N_2 . 1s 2s 2p

② He_2 / Be_2

$Be \longrightarrow 1s^2 2s^2$

$Be \longrightarrow 1s^2 2s^2$

Be_2 (molecule) $\longrightarrow \sigma 1s^2 \; \sigma^* 1s^2 \; \sigma 2s^2 \; \sigma^* 2s^2$

Bond order $= \dfrac{4-4}{2} = 0$

Since B.O of Be_2 is zero.
So Be_2 cannot exist.

Molecules having electrons less than or equal to 14 will have following configuration = $\sigma 1s$, $\sigma^* 1s$, $\sigma 2s$, $\sigma^* 2s$, $\pi 2p_y$, $\pi 2p_z$, $\sigma 2p_x$, $\pi^* 2p_y$, $\pi^* 2p_z$, $\sigma^* 2p_x$.

Molecules having electrons more than 14 will have following configuration.

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

③ N_2 / O_2

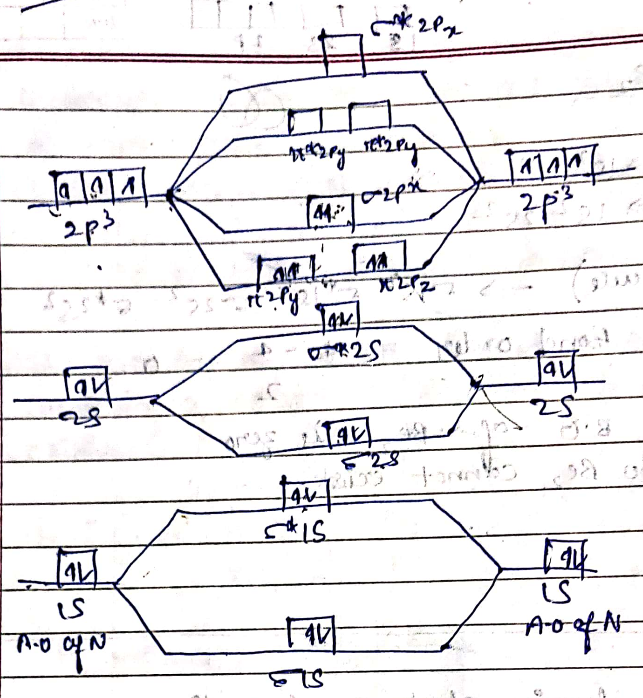
$N_2 \to$ ... $= 10$

$O_2 = 14$

$N \to 1s^2 \; 2s^2 \; 2p_x^1 \; 2p_y^1 \; 2p_z^1$

$N \to 1s^2 \; 2s^2 \; 2p_x^1 \; 2p_y^1 \; 2p_z^1$

H.W → O_2



mo of N_2

→ $B.O = \frac{10-4}{2} = \frac{6}{2} = 3$

→ Since all electrons in paired so this molecule is diamagnetic.

Homework O_2 :—

Homework Q. Arrange the following species in the increasing order of their stability:

N_2^+, N_2^-, N_2^{2+}, N_2^{2-}

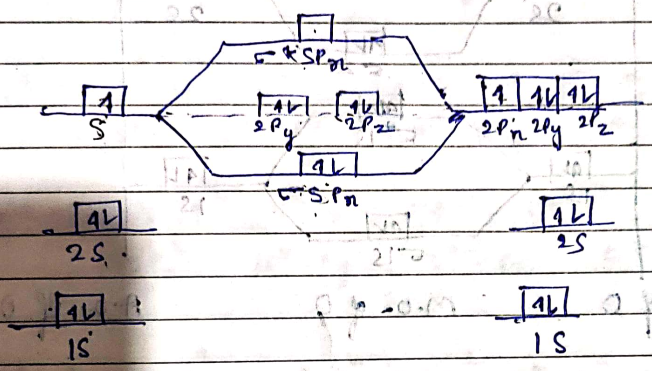
⇒ HF → It's molecular diagram same as OH^-.

$H \rightarrow 1s^1$

$F \rightarrow 1s^2\ 2s^2\ 2p_x^1\ 2p_y^2\ 2p_z^2$.

(HF) molecule :- $1s^2\ 2s^2,\ \sigma sp_x^2,\ 2p_y^2,\ 2p_z^2$
$,\ \sigma^* sp_x^0$

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

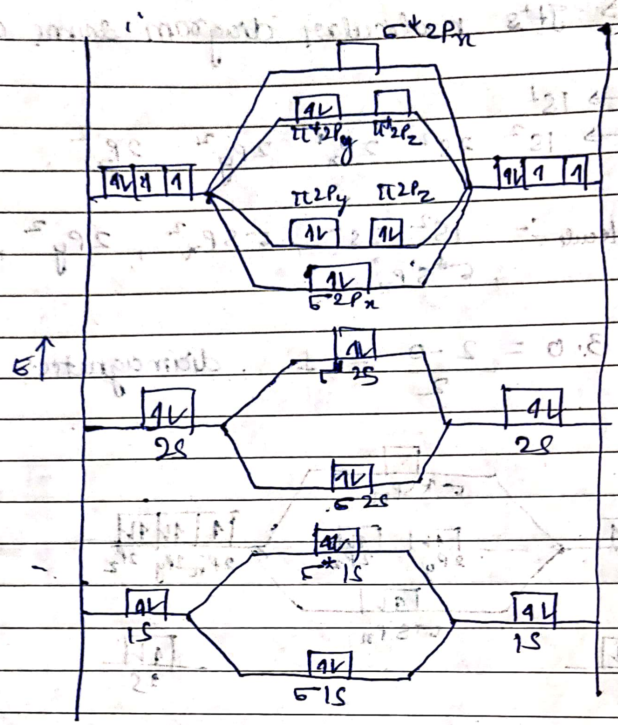


A.O of H M.O of H A.O of F

⇒ O_2 :- $_8O \rightarrow 1s^2, 2s^2$ 2px 2py 2pz

8+8=16 $_8O \rightarrow 1s^2, 2s^2$ 2px 2py 2pz

(M.O) configuration :- $\sigma 1s^2,\ \sigma^* 1s^2,\ \sigma 2s^2,\ \sigma^* 2s^2$
$,\ \sigma 2p_x^2,\ \pi 2p_y^2,\ \pi 2p_z^2,\ \pi^* 2p_y^2$
$,\ \pi^* 2p_z,\ \sigma^* 2p_x$



A.O. of O   M.O. of O   A.O. of O

Bond order $= \frac{10-6}{2} = \frac{\cancel{4}^{2}}{\cancel{2}} = 2$ (having double bond)

Since all the electrons ~~ele~~ are in paired so, it is diamagnetic.

Arrange the following species in the increasing of their stability :-
N_2^+, N_2^-, N_2^{2+}, N_2^{2-}.

Sol^n $_7N \rightarrow 1s^2\ 2s^2$ [↿|↿|↿] ($p_x\ p_y\ p_z$) } $7+7 = 14$ (sp mixing)
$_7N \rightarrow 1s^2\ 2s^2$ [↿|↿|↿] ($p_x\ p_y\ p_z$)

(M.O) configuration :- $\sigma 1s^2\ \sigma^* 1s^2\ \sigma 2s^2\ \sigma^* 2s^2\ \pi 2p_y^2$
(N_2) → $\pi 2p_z^2$, $\sigma 2p_x^2$, $\pi^* 2p_y$, $\pi^* 2p_z$, $\sigma^* 2p_x$

N_2^+ ⇒ $\sigma 1s^2$, $\sigma^* 1s^2$, $\sigma 2s^2$, $\sigma^* 2s^2$, $\pi 2p_y^2$, $\pi 2p_z^2$
$\sigma 2p_x^1$, $\pi^* 2p_y$, $\pi^* 2p_z$, $\sigma^* 2p_x$

N_2^- :- $\sigma 1s^2$, $\sigma^* 1s^2$, $\sigma 2s^2$, $\sigma^* 2s^2$, $\pi 2p_y^2$, $\pi 2p_z^2$
, $\sigma 2p_x^2$, $\pi^* 2p_y^1$, $\pi^* 2p_z$, $\sigma^* 2p_x$

N_2^{2+} :- $\sigma 1s^2$, $\sigma^* 1s^2$, $\sigma 2s^2$, $\sigma^* 2s^2$, $\pi 2p_y^2$, $\pi 2p_z^2$
, $\sigma 2p_x$, $\pi^* 2p_y$, $\pi^* 2p_z$, $\sigma^* 2p_x$

N_2^{2-} :- $\sigma 1s^2$, $\sigma^* 1s^2$, $\sigma 2s^2$, $\sigma^* 2s^2$, $\pi 2p_y^2$, $\pi 2p_z^2$
$\sigma 2p_x^2$, $\pi^* 2p_y^2$, $\pi^* 2p_z$, $\sigma^* 2p_x$

B.O. of N_2^+ :- $\frac{9-4}{2} = \frac{5}{2} = 2.5$

" of N_2^- :- $\frac{10-5}{2} = \frac{5}{2} = 2.5$

" of N_2^{2+} :- $\frac{8-4}{2} = \frac{4}{2} = 2$

" of N_2^{2-} :- $\frac{10-6}{2} = \frac{4}{2} = 2$

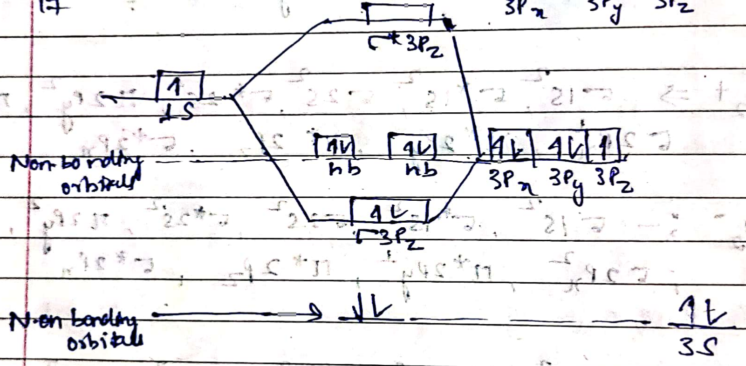
Increasing stability due to Bond order are

$N_2^{2+} < N_2^{2-} < N_2^{+} < N_2^{-}$ Ans

Malecular orbital diagram of HCl

$H \rightarrow 1s^1$

$Cl \rightarrow 1s^2\ 2s^2\ 2p^6\ 3s^2$ $\boxed{\uparrow}$ $\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow}$ ($3p_x$, $3p_y$, $3p_z$)



H (AO) HCl (MO) Cl (AOs)

$$BO = \frac{2-0}{2} = \frac{2}{2} = 1$$

All electrons in pair so it is diamagnetic Ans

Note :- Antibonding ↑ stability ↓

BAND THEORY :— (Molecular orbital theory)
(Metallic bonding)

: This theory explains metallic bonding. Metallic bonding can be defined as the bonding that holds the atom together with in a metal.

In order to explain how are large number of electrons deficient atoms are bound together in a metal, Band theory is proposed.

According to this theory :—

(i) Solids are made up of large number of atoms arranged in a regular pattern.

(2) During interaction b/w different atoms overlapping of atomic orbitals results into formation of M.O

(3) When 'n' number of atomic orbital of identical atoms in a metal interact, 'n' number of M.O are formed with a small energy difference.

(4) The group of these infinite energy levels with very small difference is called Band.

(5) The Band of energy levels occupied by the valence electrons is called Valence Band. (Homo)

(6) The next band above the valence band is called conduction band.

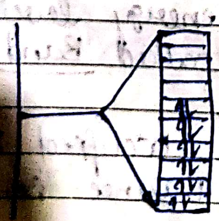
(7) The gap b/w valence and conduction Band is known as forbidden gap, forbidden zone or Band gap.

(8) A solid is a conductor if it has half filled or partially filled valence band. For ex:- (Li, Na) or A filled valence band overlapping with next higher empty Band. (Be or Mg).

(9) A solid is an insulator if it has filled valence Band, empty conduction band and a very large energy gap. for ex:- Diamond, glass, solid Neon etc.

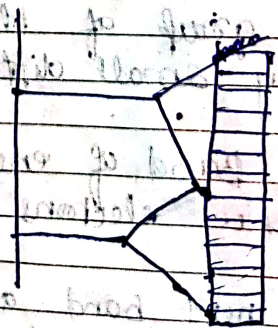
(10) A solid is a semiconductor if it has almost filled valence band, almost empty conduction Band and a very narrow energy gap. for ex:- silicon or germanium.

Conductor :-



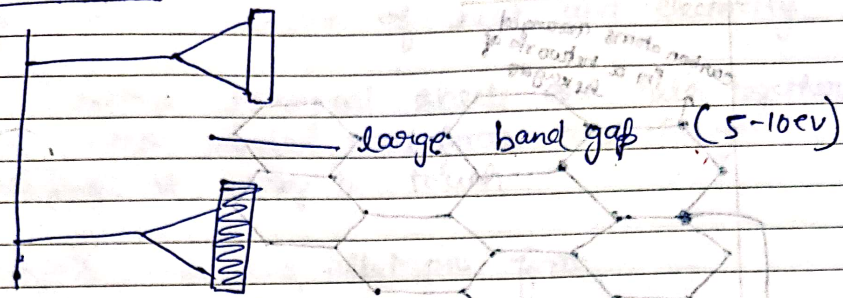
half filled or partially filled valence Band.

or

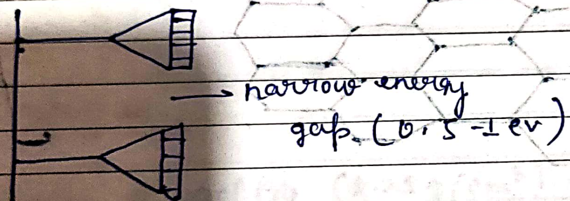


filled valence band overlapping with next higher empty band.

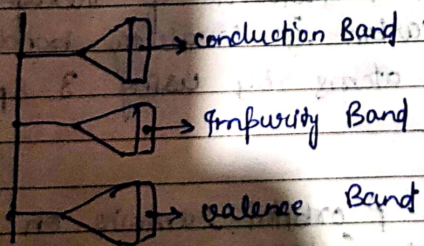
Insulators :-



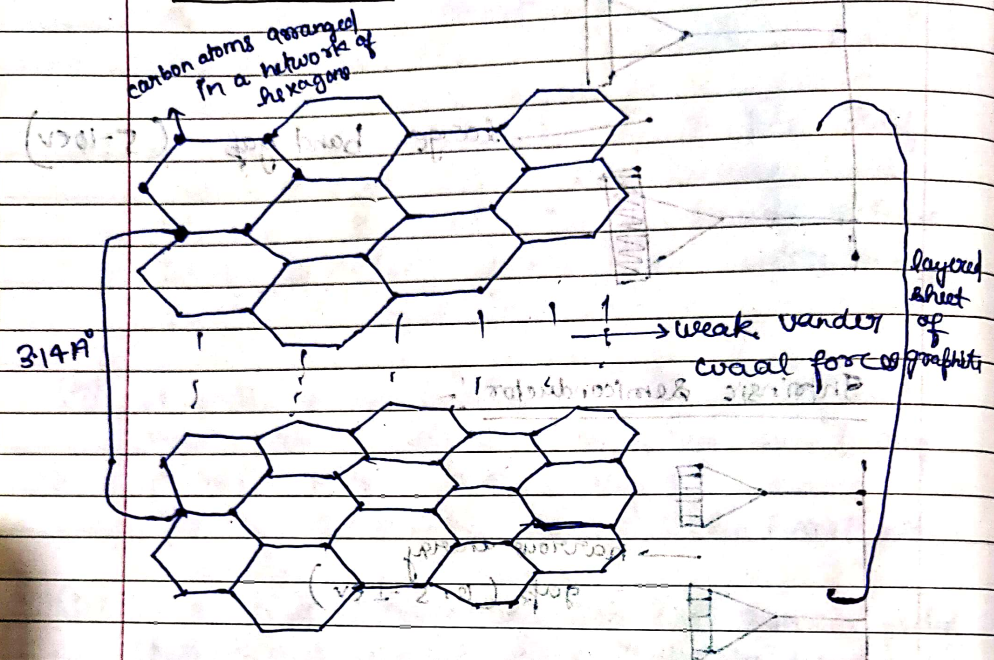
Intrinsic semiconductor :-



Extrinsic semiconductors :



GRAPHITE :- (Graphene - to write)



- Graphite has planar two dimensional sheet like structure. It consists a number of carbon atoms in a network of hexagons in which each carbon is covalently bonded to three other carbon atoms by using 3 sp^2 hybrid orbitals.

- A singly occupied p orbital remains on each carbon atom which is responsible for the overlapping of and formation of π-orbitals whose one part lies above the hexagonal plane and other parts lies below it. Thus the free electron present in these π-orbitals is free to move under the influence of applied potential difference. As a result Graphite is a good conductor of heat and electricity

:- In Graphite hexagonal sheets are held together by weak vander waal forces and therefore Graphite is soapy to touch.

:- Graphite has two allotropic form

① α - graphite
(Synthetic graphite
it exists . is count
in rhombohedral .
structure

② β-graphite
natural structure
hexagonal structure.

Properties

(i) Density of graphite ($2.25 g/cm^3$) is less than that of Diamond ($3.5 g/cm^3$)

(2) Hexagonal sheets starts sliding over one another on applying force , so graphite is soapy to touch.

(3) Melting of Graphite is high ($3700°C$) due to presence of large no. of covalent Bonds.

Application

(1) Graphite can be used as electrodes in batteries

(2) Graphite is used in pencil production

(3) As graphite is soapy to touch therefore it can be used as lubricant.

(4) Graphite blocks are used for the lining of Blast Furnaces in iron production.

Fullerene (Introduction)

→ In 1990, two scientists W. Kratschmer and D. Hoffman discovered another allotropes of carbon i.e. fullerene. For this discovery they was awarded ~~too~~ with Noble prize.

→ Fullerene consists of large number of carbon atoms in elliptical, spherical or in cylindrical manner. For example, C-20, C-24, C_{28}, C_{36}, C_{60} ----- C_{70} etc.

→ C_{60} is the most important and also known as buckminster fullerene in the honour of an Architect who designed a dome-shaped structure based on pentagon and hexagon. The shape of C-60 resembles to that to that structure designed by Buckminster fullerene.

PREPARATION :-

→ When ~~The~~ electricity is passed through Graphite electrodes in presence of Argon-gas at a pressure of 0.05 to 0.1 Atm, soot is produced.

C_{60} is extracted from soot by chromatographic technique using benzene as solvent.

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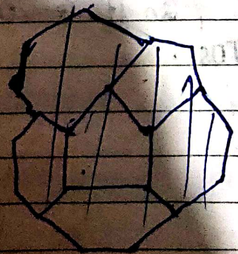
STRUCTURE :-

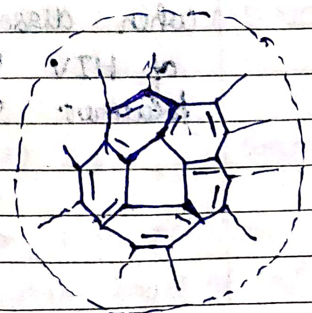
C_{60} is a cage like molecule, with an ~~Icoso~~ Icosahedron geometry. (It is a Polygon with 60 - vertices and 32 faces, 12 of which are pentagonal and 20 are hexagonal).

In C_{60} each carbon is sp^2 hybridised and the valency of each carbon atom is satisfied two single and one-double bond. In C-60 each pentagon are surrounded by 5 hexagons and no two pentagons are adjacent.

The arrangement of 5 and 6 member rings gives it soccer ball shaped. so C_{60} is also known as ~~Buckiel ball~~, 'buckyball'.

As it has FCC structured, C_{60} has tetrahedral and octahedral holes, Due to absence of free electrons C_{60} is an insulator but can be made conducting by doping with Alkali metals atom.





Structure of CO.

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Properties :-

(1) It is a mustard coloured solid, other fullerenes are black powdery material.

(2) It gives magenta coloured solution with benzene.

(3) It is highly thermally stable.

(4) It is highly photosensitive as it gets polymerise on exposure to strong UV light

(5) C_{60} is an insulator but can be made conducting by doping with alkali metal atom.

Applications

(1) In batteries
(2) As charge carriers
(3) In electronic and microelectronic devices.
(4) A derivation of C_{60} synthesized by Wudl when dissolve in water, inhibit the activity of HIV virus, so it is used in the treatment of AIDS.

LIQUID CRYSTAL / MESOMORPHIC state

→ There are certain solids which can when heated undergo two phase changes one after the other.

→ They first convert into turbid liquide at a particular temperature and then into a clear liquid on heating at particular temperature.

This process can be reversed on cooling at room temperature.

→ Substances showing above behaviour are known as Liquid crystals but according to G. Friedal they can be called as Mesomorphic state (intermediate form)

$$\text{Solid} \underset{}{\overset{\text{heat}}{\rightleftharpoons}} \text{Turbid liquid} \underset{}{\overset{\text{heat}}{\rightleftharpoons}} \text{clear liquid}$$

→ Substances showing above ~~are~~ behaviour are long chain organic molecules having groups like $-OR$, $-COOR$ at the end of chain and having groups like $-C=C-$, $-C=N-$, $-N=NO-$ in the middle of the chain.

→ Cholesteryl Benzoate ($C_6H_5COO\,C_{27}H_{45}$) was first solid discovered to have this peculiar properties. It convert into turbid liquid at 145°C and then into clear liquid at 178°C.

→ The temperature at which solid convert into turbid liquid is called transition point and the temperature at which turbid liquid changes into clear liquid is called melting point

Ex- Cholesteryl Benzoate $\underset{\longleftarrow}{\xrightarrow{145^\circ C}}$ Turbid liquid $\underset{\longrightarrow}{\xleftarrow{178^\circ C}}$ clear liquide

(145°C → transition point; 178°C → melting point)

CLASSIFICATION OF LIQUID CRYSTALS

① Lyotropic liquid crystals (concentration dependent
② Thermotropic liquid crystals (Temperature dependent)

- Nematic liquid crystal
- Smectic liquid crystal
- ~~Chole~~ Cholesteric liquid crystal

Nematic Liquid Crystal

It is the simplest form of liquid crystal in which crystal molecules have random positional order and are free to move. However in Nematic liquid crystals Molecules have fixed orientation order. Liquid crystals in this phase have thread-like appearance under microscope.

They are also affected by strong magnetic field as when they are in magnetic field, they appear clear and become turbid again when magnetic field is cut off

Ex- p-azoxy-phenetole

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(2) Smectic Liquid crystal

→ They are characterized by fixed orientational order and somewhat fixed positional order of molecules.

→ They are present in layers in which movement of molecules, within the layer is restricted but they can be move as a whole with layer. Due to less interaction between layers, they are soapy to touch and can be used as Lubricant.
for ex:- P-azoxy anisole.

Cholesteric Liquid crystal

• They have Helical structure like DNA and are present in Layers. In this crystals molecules have random positional order ~~and~~ but fixed orientation -al order. As the distance b/w the layers are temperature dependent, so these crystals are used in making temperature sensing device like thermometer. for example:- Cholesteryl Benzoate

Applications

(1) Nematic liquid crystals are used in LCD Screen.

(2) Smectic Liquid crystal are used as Lubricant.

(3) Cholesteric Liquid crystal are used in making temperature sensing devices like thermometer.

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(4) Cholesteryl Benzoate are used in the diagnosis of tumours in circulatory system.

(5) Liquid crystals are used as solvent during spectroscopic study of certain molecules.