MODULE 1

ATOMIC AND MOLECULAR STRUCTURE

Molecular orbitals of diatomic molecules. Band theory of solids, Liquid crystal and its applications. Point defects in solids. Structure and applications of Graphite and Fullerenes. Concepts of Nanomaterials and its application.

Contents

1.CHEMICAL BOND

Chemical bonding, any of the interactions that account for the association
of atoms into molecules, ions, crystals, and other stable species that make up the familiar
substances of the everyday world. When atoms approach one another, their nuclei
and electrons interact and tend to distribute them in space in such a way that the
total energy is lower than it would be in any alternative arrangement. If the total energy
of a group of atoms is lower than the sum of the energies of the component atoms, they
then bond together and the energy lowering is the bonding energy.

A chemical bond is a sort of attraction which keeps the two atoms together. These chemical
bonds are what keep the atoms together in the resulting from the loss, gain, or sharing of
electrons between two atoms/molecules. Thus depending upon the variety of force, there
may be variety of chemical bonds.

## 1.1 REASONS FOR THE FORMATION OF A CHEMICAL BOND

1.1.1 Energy concept: When two atoms approach each other, the attractive and repulsive forces
operate between them. The distance at which the attractive forces overweigh the repulsive forces is
known as the bond distance, the potential energy of the system is minimum and the bond is said to
be formed.
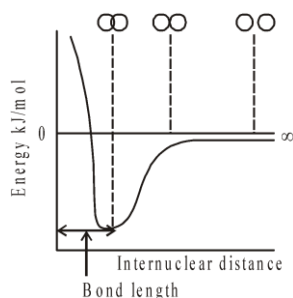
1.1.2 Lewis and Langmuir (Octet Rule) : Concept of stable electronic configuration.
Atoms enter into chemical bonding to acquire the stable inert gas electronic configuration. They can
do so by losing, gaining or sharing of electrons.

1.1.3 Lewis symbols : The electrons present in the outermost energy level of an atoms and known
as valence electrons. Only valence electrons are involved in the combination of two atoms. The
representation of valence electrons on an atom called Lewis Symbol eg-
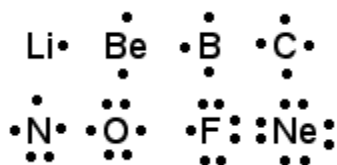
1.2 TYPES OF CHEMICAL BOND:

Primary bond- Primary bonds are formed when the bonding process involves a transfer or sharing of electrons. Primary bonds are those which are strong in nature. They have electronic attractions and repulsions just like secondary bonds but in equilibrium they are stronger than the later. They are broadly classified into three types:

- Ionic bonds

- Covalent bonds

- Metallic bonds.

- Coordinate bond

1.2.1 IONIC BOND

Ionic bond is formed by the complete transference of one or more valence electrons of one atom to the valence shell of the other atom. Both atoms are converted into ions and have the electronic configuration of nearest noble gases. The electrostatic attraction between these oppositely charged ions, which always tends to decrease the potential energy of the system is known as the ionic bond. Consider the formation of KCl. The electronic configuration of K, Cl and their ions (K^+ and Cl^-) are given below
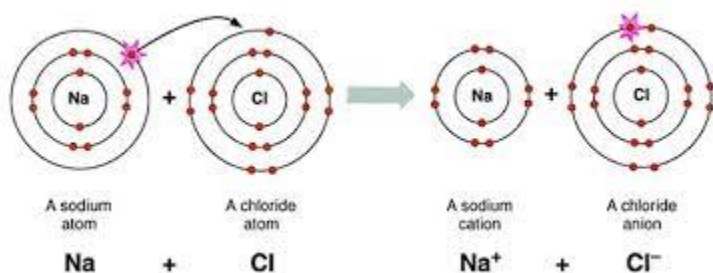
K (19) $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1$

K^+(18) $1s^2, 2s^2, 2p^6, 3s^2, 3p^6$ Inert gas (Ar) configuration

Cl (17) $1s^2, 2s^2, 2p^6, 3s^2, 3p^5$

Cl^- (18) $1s^2, 2s^2, 2p^6, 3s^2, 3p^6$ Inert gas (Ar) configuration

$K^+ + Cl^- \rightarrow KCl$

The number of electrons lost or gained by an atom represents the electrovalence of the atom.

A sodium atom + A chloride atom → A sodium cation + A chloride anion

Na + Cl → Na⁺ + Cl⁻

PROPERTIES OF IONIC COMPOUNDS

The important properties are as follows

1. **Crystal structure :** The crystalline ionic compounds have well defined crystal structure or crystal lattice eg in NaCl each Na^+ is surrounded by six Cl^- ions and vice versa
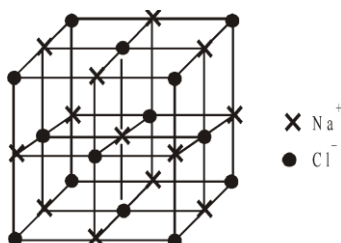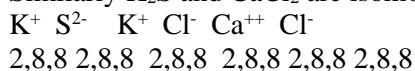

Cubical structure of sodium chloride crystal

× Na⁺
● Cl⁻

2.   **Melting and boiling points :** Ionic compounds have high m.pt and b.pt due to powerful electrostatic force between ions.

3.   **Solubility :** They are generally soluble in polar solvents (having high value of dielectric constant). The solubility of ionic compounds decreases with increase in covalent character of ionic compounds. It is also governed by-

a.   **Lattice energy :** More the lattice energy, lesser is the solubility, eg. sulphates and phosphates of Ba and Sr are insoluble in water due to high lattice energy.

b.   **Heat of hydration :** More the heat of hydration, more is the solubility. eg $AlCl_3$ though covalent in nature is soluble in water due to high value of heat of hydration.

4.   **Electrical conductivity :** In solid state they do not conduct electricity since there is no free movement of electrons but in molten state and in solution they conduct electricity.

5.   **Isomorphism :** NaF and MgO are isomorphous due to similar electronic structure

$$\underset{2,8}{Na^+} \quad \underset{2,8}{F^-} \quad \underset{2,8}{Mg^{++}} \quad \underset{2,8}{O^{--}}$$
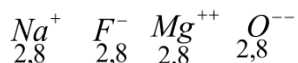
Similarly K_2S and $CaCl_2$ are isomorphous
K^+ S^{2-} K^+ Cl^- Ca^{++} Cl^-
2,8,8 2,8,8 2,8,8 2,8,8 2,8,8 2,8,8

1.2.2 COVALENT BOND :

According to G. N. Lewis atoms may also combine by sharing of electrons present in their outermost shells and attain noble gas electronic configuration. One shared pair of electrons constitute a single bond, two electron pairs constitute a double bond and so on. The bonds thus formed are known as covalent bonds.
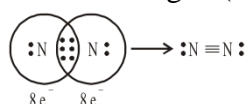
EXAMPLES OF COVALENT COMPOUNDS

1.   Chlorine (Cl_2)
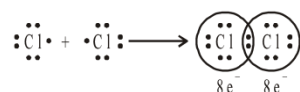
2.   Carbon dioxide (CO_2)
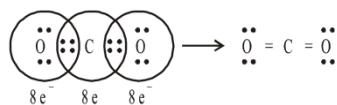
3.   Nitrogen (N_2)

PROPERTIES OF COVALENT COMPOUNDS

1.   **Physical state** - They may be gases, liquids or solids

2.   **Crystal structure** - They may exist as simple molecules held together by weak forces, giant molecules united by covalent link eg diamond, silicon carbide, alumina, aluminium nitride etc and can have layer structure. eg graphite.

3.   **Solubility** - Generally soluble in non polar solvents.

4.   **Melting/ boiling points** - Low as compared to ionic compounds.

5.   **Electrical conductivity** - Being non electrolytes they do not conduct electricity, graphite does due to presence of free electrons.

6.   **Stereo-isomerism** - They exhibit structural and stereo-isomerism both

HYBRIDISATION

Hybridisation is the redistribution of energy levels at the time of formation of molecules. It may also be defined as intermixing of atomic orbitals of nearly the same energy and resulting in the formation of new atomic orbitals same in number and identical in all respects (shape, energy and size). The new atomic orbitals are known as hybrid atomic orbitals.

The completely filled or half filled atomic orbitals can take part in hybridisation and hybrid atomic orbitals form stronger bonds.

METHOD FOR FINDING THE TYPE OF HYBRIDISATION

Apply the following formula to find the hybridisation of central atom.

$$\frac{1}{2}\left(\begin{array}{l}\text{Number of valence electrons of central atom} \\ +\text{ number of monovalent atoms attached to it} \\ +\text{ negative charge if any} - \text{positive charge if any}\end{array}\right) = z$$

Value of z 2 3 4 5 6   7

Hybridisation sp sp^2 sp^3 sp^{3}d sp^{3}d^2 sp^{3}d^3

Examples :

1.　　　Hybridisation of NH_3 = [5 + 3 + 0 - 0] = 4; sp^3
2.　　　Hybridisation of H_2O = [6 + 2 + 0 - 0] = 4; sp^3
3.　　　Hybridisation of SO_3 = [6 + 0 + 0 - 0] = 3; sp^2
4.　　　Hybridisation of SO_4^{2-} = [6 + 0 + 2 - 0] = 4; sp^3
5.　　　Hybridisation of CO_3^{2-} = [4 + 0 + 2 - 0] = 3; sp^2
6.　　　Hybridisation of PCl_5 = [5 +5 + 0 - 0] = 5; sp^{3}d
7.　　　Hybridisation of SF_6 = [6 + 6 + 0 - 0] = 6; sp^{3}d^2

**Note :** Species having same hybridisation are isostructral in nature.

1.2.3 COORDINATE COVALENT BOND OR DATIVE BOND

When both the electrons for sharing between two atoms are contributed by one atom only the bond formed is known as coordinate bond or dative bond.

The atom donating the pair of electrons is called donor and the atom which accepts the pair of electrons is called acceptor. The compounds containing coordinate bonds are known as coordination compounds. The bond is represented by an arrow ($\rightarrow$) pointing head towards the acceptor.

Some examples are:

1.　　　Formation of SO_2
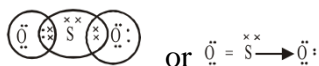
2.　　　Formation of SO_3
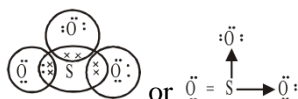
3.　　　Formation of Hydroxonium ion

4.　　　NH_3 and BF_3 form addition product by Coordinate covalent bond

```
      H      F
      |      |
H  —  N  :→  B  —  F    o r   H ₃ N . B F₃
      |      |
      H      F
```
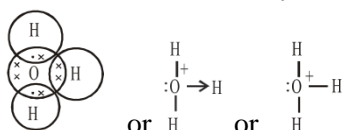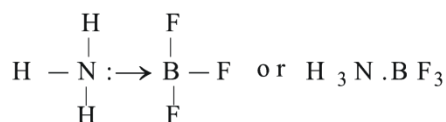
PROPERTIES OF COORDINATE COMPOUNDS

Coordinate compounds have volatile character in between ionic and covalent compounds. Other properties like solubility, electrical conductivity and stereo-isomerism are similar to covalent compounds.
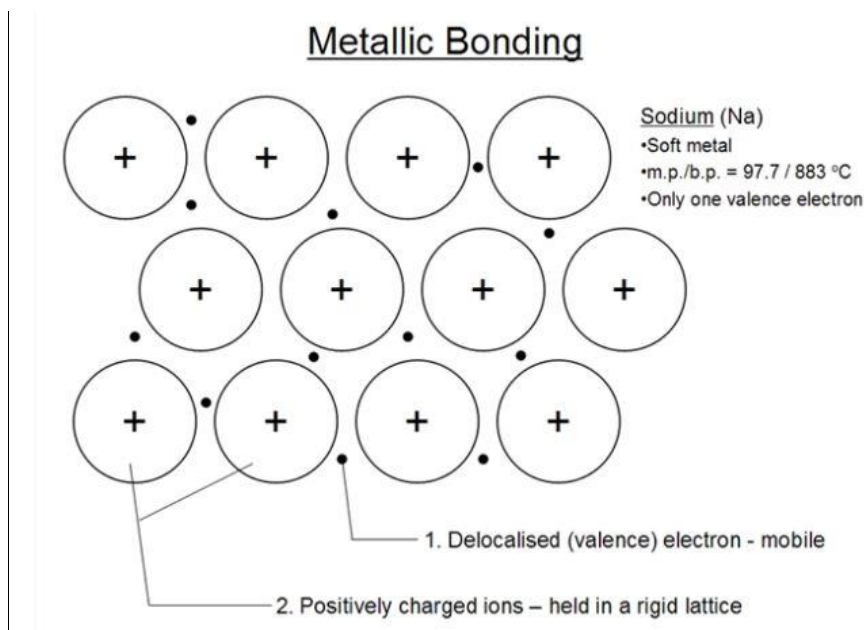
1.2.4   METALLIC BOND

Metallic bond' is a term used to describe the collective sharing of a sea of valence electrons between several positively charged metal ions. Metallic bonding is a type of chemical bonding and is responsible for several characteristic properties of metals such as their shiny lustre, their malleability, and their conductivities for heat and electricity.

Both metallic and covalent bonding can be observed in some metal samples. For example, covalently bonded gallium atoms tend to form crystal structures that are held together via metallic bonds. The mercurous ion also exhibits metallic and covalent bonding.

Structure of a Metallic Crystal
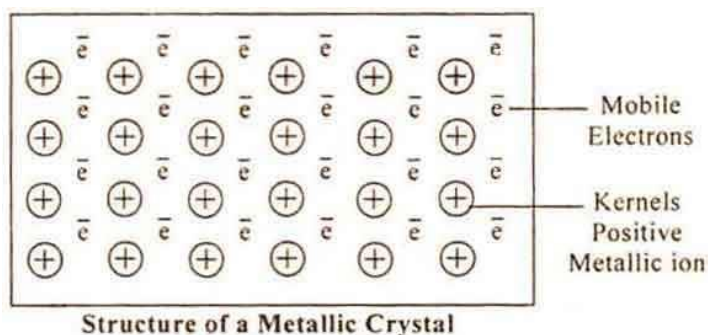
The factors that affect the strength of a metallic bond include:

- Total number of delocalized electrons.
- Magnitude of positive charge held by the metal cation.
- Ionic radius of the cation
- Metallic bonds are not broken when the metal is heated into the melt state. Instead, these bonds are weakened, causing the ordered array of metal ions to lose their definite, rigid structure and become liquid. However, these bonds are completely broken when the metal is heated to its boiling point.

- Example – Metallic Bonding in Sodium

- The electron configuration of sodium is $1s^2 2s^2 2p^6 3s^1$; it contains one electron in its valence shell. In the solid-state, metallic sodium features an array of Na^+ ions that are surrounded by a sea of 3s electrons. However, it would be incorrect to think of metallic sodium as an ion since the sea of electrons is shared by all the sodium cations, quenching the positive charge.

- An illustration describing the metallic bonding in sodium is provided below.

Metallic Bonding

Sodium (Na)
•Soft metal
•m.p./b.p. = 97.7 / 883 °C
•Only one valence electron

1. Delocalised (valence) electron - mobile

2. Positively charged ions – held in a rigid lattice

The softness and low melting point of sodium can be explained by the relatively low number of electrons in the electron sea and the relatively small charge on the sodium cation. For example, metallic magnesium consists of an array of Mg^{2+} ions. The electron sea here contains twice the number of electrons than the one in sodium (since two 3s electrons are delocalized into the sea). Due to the greater magnitude of charge and the greater electron density in the sea, the melting point of magnesium (~650oC) is significantly higher than that of sodium.

CONSEQUENCES OF METALLIC BOND

1.   **Electrical conductivity** - It is due to presence of mobile valence electrons.

2.   **Thermal conductivity** - On heating one part of metal, the K.E. of electrons is increased and they conduct heat to the other parts of the metal.

3.   **Metallic lustre** - The mobile electrons are promoted to excited states by absorption of light and on coming back from the excited state light of all wavelengths in the visible region are emitted. The surface therefore emits metallic lustre.

4.   **Malleability** - Metals can be made thin sheets

5.   **Ductility** - Metals can be drawn into wires since metal kernels can easily be shifted.

6.   **Electrical conductivity decreases with temperature** - It is due to random motion of mobile electrons which increases with increase of temperature.

Secondary bond- Secondary bonds are formed from the subtle attraction forces between positive and negative charges. Secondary bonds are bonds of a different kind to the primary ones. They are weaker in nature and are broadly classified as:

•   Van der Waal's forces

•   Hydrogen bonds.
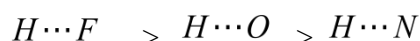
1.2.5   HYDROGEN BOND

It may be defined as the force of attraction existing between hydrogen atom covalently bonded to highly electronegative atom (N, O or F) and the electronegative atom belonging to another molecule of the same or different substance. It is represented by dotted lines

H–F .... H–F .... H–F
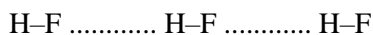
The chains possess a **Zig-Zag** structure
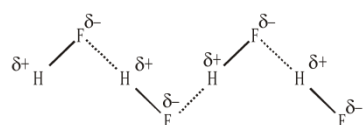
Hydrogen bond is purely electrostatic in nature. It is a weak bond, the strength of the strongest being about 5 - 10 kcal per mole. The more the electronegativity of atom involved in H - bonding, the more is the bond strength eg.

$$H \cdots F \quad > \quad H \cdots O \quad > \quad H \cdots N$$

10 kcal/mole >   7 kcal/mole > 2.0 kcal/mole

TYPES OF HYDROGEN BONDS

Hydrogen bond is of two types

1.   Intermolecular H-bonding (Association) -. When hydrogen bonding occurs between to atoms of different molecule then it is called intermolecular hydrogen bonding. For such bonding one molecule should have a partially positive hydrogen as acceptor atom and another should have a partially negative or donor atom. As for example, hydrogen bonding between aldehyde and water molecule has given below: H–bonding involving two or more molecules.

Intermolecular hydrogen bonding between water and aldehyde molecule
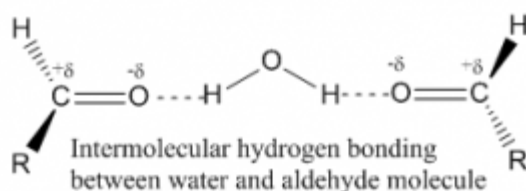
2.   Intramolecular H-bonding (Chelation)-. When hydrogen bonding occurs between two partially charged atoms of same molecule that is called intramolecular hydrogen bonding. This occurs when two functional groups are present in same molecule and they are in such way that can attract each other to form hydrogen bond. For example salicylic acid has two functional groups alcohol and carboxylic acid. Here intramolecular hydrogen bonding occurs between the hydrogen atom of alcohol group and the oxygen atom of carboxylic acid group. H–bonding taking place within single molecule.
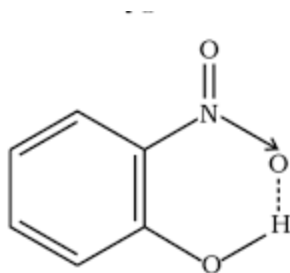
> Intramolecular hydrogen bonding in
> o-nitrophenol molecule

1.2.6   VAN DER WAAL'S FORCES

Attractive forces between uncharged molecules are known as van der Waals forces. These forces may be divided into three groups

1.   Dispersion or London forces. These are due to transient polarisation.
2.   Dipole-dipole attraction. These are due to permanent polarisation.
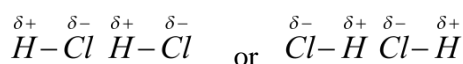3.   Dipole-induced dipole forces

LONDON FORCES

The negative electrons in a neutral molecule are balanced by the positive charges on the nucleus. Since the electrons are in motion the centre of density of the electrons does not coincide continuously with the centre of density of positively charged nuclei, the molecules acquire an electric dipole. Polarised molecules exert an attraction for other molecules having a dipole. Consider the case of helium.

Non polar   Polarised
  atom   atom

Attraction between polarised atom
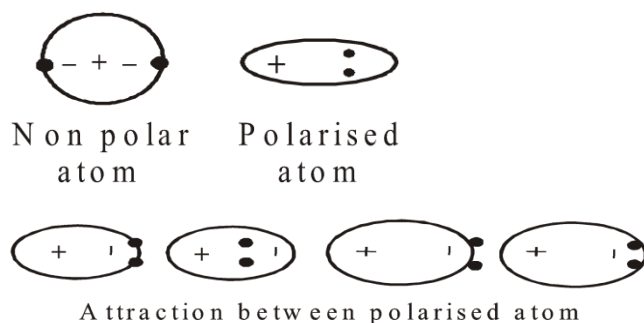
*   The greater the polarizability of a molecule, the stronger are the London forces.
*   The polarizability increases with number of electrons and their distance from the nucleus.
*   These forces are operative over a very short range.
*   The inert gases have weak van der Waals forces of attraction
*   The straight chain hydrocarbons boil at higher temperature than isomeric branched chain hydrocarbons due to greater magnitude of van der Waal's forces of attraction.

DIPOLE-DIPOLE ATTRACTION

It is the attraction between the positive end of the one molecule and negative end of the another molecule

$$\overset{\delta+}{H}-\overset{\delta-}{Cl}\ \overset{\delta+}{H}-\overset{\delta-}{Cl}$$ or $$\overset{\delta-}{Cl}-\overset{\delta+}{H}\ \overset{\delta-}{Cl}-\overset{\delta+}{H}$$

This type of interaction is called dipole - dipole interaction. The force of dipole - dipole attraction is inversely proportional to fourth power of their separation of distance r. $F=\dfrac{1}{r^4}$. The dipole dipole attractions in gaseous molecules are particularly small since the gas molecules are in continuous motion. This attraction increases the m.pt. and b.pt. of substances and makes their liquefaction easy.

DIPOLE-INDUCED DIPOLE ATTRACTION

The attractive forces operate between polar molecules having permanent dipole and non-polar molecules. The polarity in the non-polar molecules is induced by the polar molecule

Polar molecules   Non-polar molecules
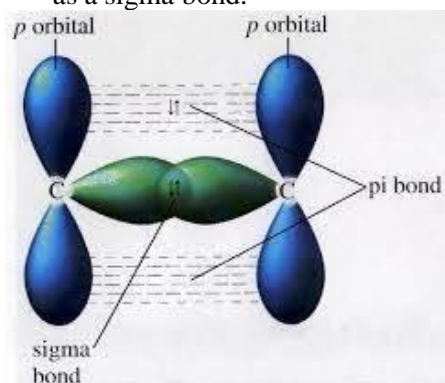
1.3 VALENCE BOND THEORY

Heitler and London introduced this theory. According to the valence bond theory, electrons in a molecule occupy atomic orbitals rather than molecular orbitals. The atomic orbitals overlap on the bond formation and the larger the overlap the stronger the bond.

This theory focuses on the concepts of electronic configuration, atomic orbitals (and their overlapping) and the hybridization of these atomic orbitals. Chemical bonds are formed from the overlapping of atomic orbitals wherein the electrons are localized in the corresponding bond region.

The important postulates of the valence bond theory are listed below.

- Covalent bonds are formed when two valence orbitals (half-filled) belonging to two different atoms overlap on each other. The electron density in the area between the two bonding atoms increases as a result of this overlapping, thereby increasing the stability of the resulting molecule.
- The presence of many unpaired electrons in the valence shell of an atom enables it to form multiple bonds with other atoms. The paired electrons present in the valence shell do not take participate in the formation of chemical bonds as per the valence bond theory.
- Covalent chemical bonds are directional and are also parallel to the region corresponding to the atomic orbitals that are overlapping.
- Sigma bonds and pi bonds differ in the pattern that the atomic orbitals overlap in, i.e. pi bonds are formed from sidewise overlapping whereas the overlapping along the axis containing the nuclei of the two atoms leads to the formation of sigma bonds.

- The overlapping of two half-filled valence orbitals of two different atoms results in the formation of the covalent bond. The overlapping causes the electron density between two bonded atoms to increase. This gives the property of stability to the molecule.

- In case the atomic orbitals possess more than one unpaired electron, more than one bond can be formed and electrons paired in the valence shell cannot take part in such a bond formation.

- A covalent bond is directional. Such a bond is also parallel to the region of overlapping atomic orbitals.

- Based on the pattern of overlapping, there are two types of covalent bonds: sigma bond and a pi bond. The covalent bond formed by sidewise overlapping of atomic orbitals is known as pi bond whereas the bond formed by overlapping of atomic orbital along the inter nucleus axis is known as a sigma bond.

1.3.1 LIMITATIONS OF VALENCE BOND THEORY

- It fails to explain the magnetic properties of some molecules e.g oxygen
- It fails to explain the tetravalency of carbon.
- No insight offered on the energies of the electrons.
- It does not provide a quantitative explanation as to why certain complexes are inner orbital complexes and the others are outer orbital complexes for the same metal. For example, [Fe(CN)6]4- is diamagnetic (low spin) whereas [FeF6]4- is paramagnetic (high spin).
- No distinction between weak and strong ligands.
- No explanation for the colour exhibited by coordination compounds.

1.4. MOLECULAR ORBITAL THEORY OR HUND- MULLIKEN THEORY

The molecular orbital theory was given by the scientists **Hund** and **Mulliken** in the year 1932. According to this theory –

1.The atomic orbitals combine to form the molecular orbitals. The number of molecular orbitals formed re equal to the number of atomic orbitals involved and they belong to the molecule.

2.Atomic orbitals of comparable energy and proper symmetry combine to form molecular orbitals

3.The number of molecular orbital formed is equal to the number of combining atomic orbitals.

4.When two atomic orbitals (AO's) combine together two molecular orbitals (MO's) are formed. One molecular orbital possess higher energy than corresponding atomic orbitals and is called anti bonding molecular orbital (ABMO) and the other has lower energy and is called bonding molecular orbitals (BMO)

5.The molecular orbitals are formed by LCAO method (linear combination of atomic orbitals) i.e. by addition or subtraction of wave functions of individual orbitals ,thus

$$\Psi\ MO = \Psi_A \pm \Psi_B$$

$$\Psi\ b = \Psi_A + \Psi_B$$

$$\Psi\ a = \Psi_A - \Psi_B$$

6.The probability of finding an electron in bonding and antibonding molecular orbital will be given by:

$$\psi^2 = (\psi_A + \psi_B)^2 = \psi_A^2 + \psi_B^2 + 2\psi_A\psi_B$$

$$\psi^2 = (\psi_A - \psi_B)^2 = \psi_A^2 + \psi_B^2 - 2\psi_A\psi_B$$

7.Molecular orbital of lower energy is known as bonding molecular orbital and of higher energy is known as antibonding molecular orbital.

8. The electrons are filled in the increasing energy of *MO* which is in the order given below

(a)
$$\sigma 1s, \sigma^* 1s, \sigma 2s, \sigma^* 2s, \sigma 2p_z, \pi 2p_y \quad \pi^* 2p_y, \sigma^* 2p_z$$
$$\pi 2p_z, \quad \pi^* 2p_z$$

(b)
$$\sigma 1s, \sigma^* 1s, \sigma 2s, \sigma^* 2s, \quad \pi 2p_y, \quad \sigma 2p_z,$$
$$\pi^* 2p_z$$

9.In molecules electrons are present in molecular orbitals. The electron filling is in accordance with Pauli's exclusion principle, Aufbau principle and Hund's rule.

- Aufbau's principle: Molecular orbitals are filled in the increasing order of energy levels.
- Pauli's exclusion principle: In an atom or a molecule, no two electrons can have the same set of four quantum numbers.
- Hund's rule of maximum multiplicity: Pairing of electrons doesn't take place until all the atomic or molecular orbitals are singly occupied.
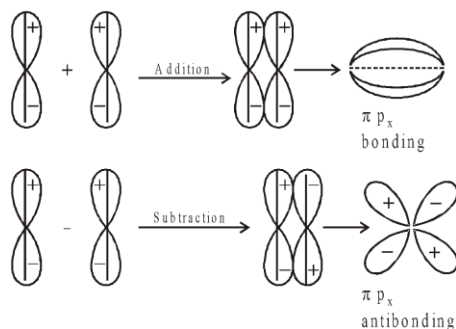
10.Their shape is governed by the shape of atomic orbitals according to LCAO:eg by s - s and p - p overlapping we have.
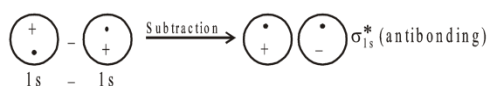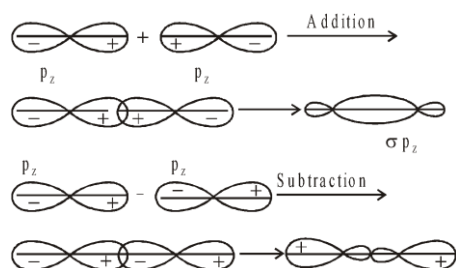
$p_x + p_x$ or $p_x - p_x$ and $p_y + p_y$ or $p_y - p_y$ overlap to form bond

$p_x + p_x$

πp_x
bonding

πp_x
antibonding

$p_z + p_z$ form σ bond and their combination is according to inter-nuclear distance.

11.. Atoms have atomic orbitals with one nuclei and Molecules have molecular orbitals with n nuclei. Thus, atoms are monocentric while molecules are polycentric.

12 Bond order $= \dfrac{1}{2}$ [Number of bonding electrons - Number of antibonding electrons]

13. Molecules or ions having electrons unpaired are paramagnetic while those with all paired electrons are diamagnetic in nature.

1.4.1 MOLECULAR ORBITAL DIAGRAM(ENERGY LEVEL DIAGRAM)

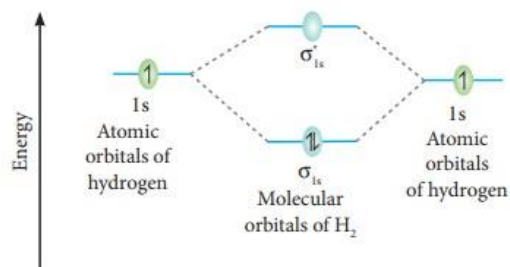Bonding in some Homonuclear di-atomic molecules

Fig 10.30 MO Diagram for H_2 molecule

Molecular orbital diagram of hydrogen molecule (H_2)
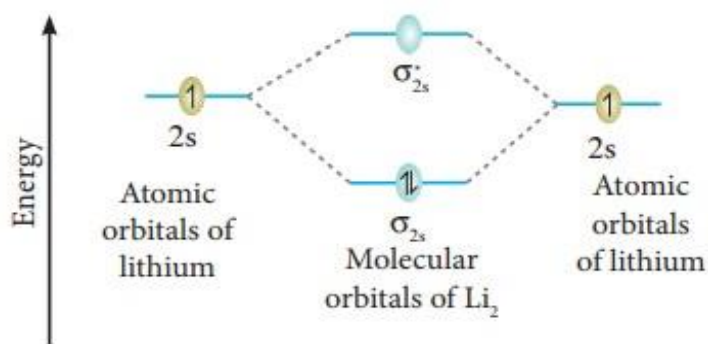
Electronic configuration of H atom $1s^1$

Electronic configuration of H_2 molecule σ_{1s}^2

Bond order $= \dfrac{N_b - N_a}{2} = \dfrac{2-0}{2} = 1$

Molecule has no unpaired electrons hence it is diamagnetic.

Fig 10.31 MO Diagram for Li₂ molecule

Molecular orbital diagram of lithium molecule (Li$_2$)

Electronic configuration of Li atom $1s^2 2s^1$

Electronic configuration of Li$_2$ molecule $\sigma_{1s}^2, \sigma_{1s}^{*2}, \sigma_{2s}^2$

Bond order $= \dfrac{N_b - N_a}{2} = \dfrac{4-2}{2} = 1$

Molecule has no unpaired electrons hence it is diamagnetic.

Fig 10.32 MO Diagram for B₂ molecule

Molecular orbital diagram of boron molecule (B_2)

Electronic configuration of B atom $1s^2\, 2s^2\, 2p^1$

Electronic configuration of B_2 molecule $\sigma_{1s}^2, \sigma_{1s}^{*2}, \sigma_{2s}^2, \sigma_{2s}^{*2}, \pi_{2p_y}^1, \pi_{2p_z}^1$

Bond order $= \dfrac{N_b - N_a}{2} = \dfrac{6-4}{2} = 1$

Molecule has two unpaired electrons hence it is paramagnetic.

Fig 10.33 MO Diagram for C_2 molecule

Molecular orbital diagram of carbon molecule (C_2)

Electronic configuration of C atom $1s^2 2s^2 2p^2$

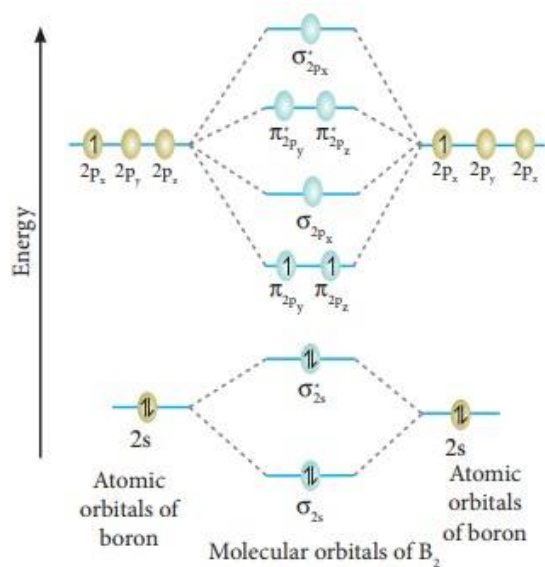Electronic configuration of C_2 molecule
$\sigma_{1s}^2, \sigma_{1s}^{*2}, \sigma_{2s}^2, \sigma_{2s}^{*2}, \pi_{2p_y}^2, \pi_{2p_z}^2$

Bond order $= \dfrac{N_b - N_a}{2} = \dfrac{8-4}{2} = 2$

Molecule has no unpaired electrons hence it is diamagnetic.

Fig 10.34 MO Diagram for N_2 molecule

Molecular orbital diagram of nitrogen molecule (N_2)

Electronic configuration of N atom $1s^2 2s^2 2p^3$

Electronic configuration of N_2 molecule $\sigma_{1s}^2, \sigma_{1s}^{*2}, \sigma_{2s}^2, \sigma_{2s}^{*2}, \pi_{2p_y}^2, \pi_{2p_z}^2 \sigma_2^2 px$

Bond order $= \dfrac{N_b - N_a}{2} = \dfrac{10 - 4}{2} = 3$

Molecule has no unpaired electrons hence it is diamagnetic.

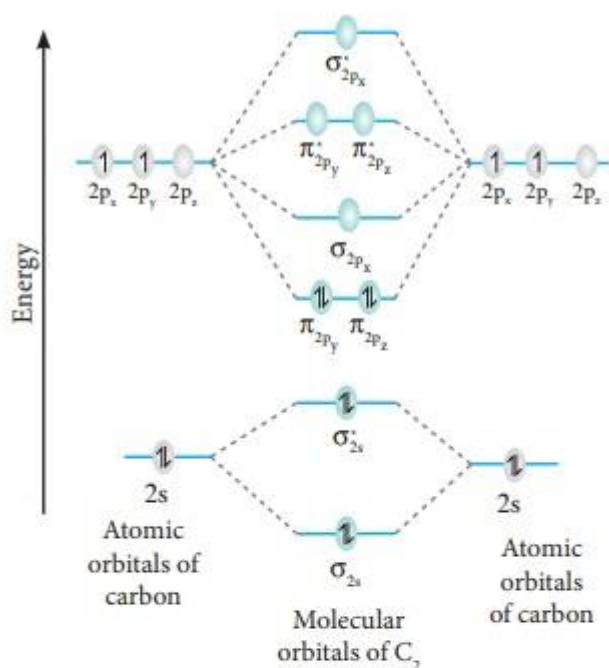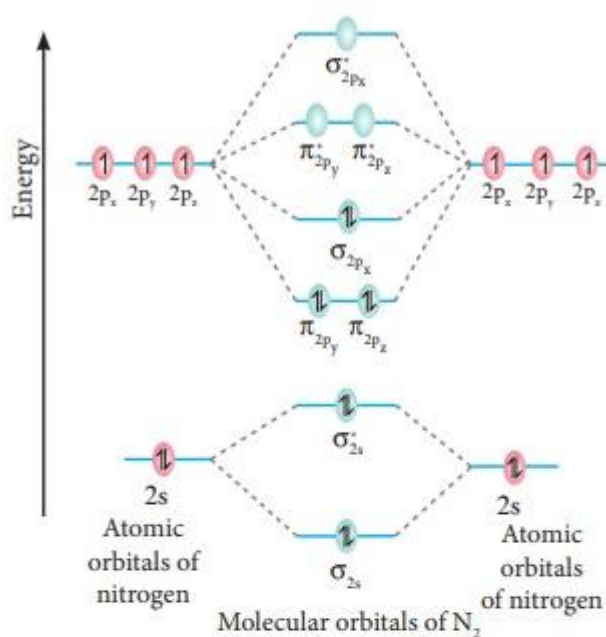Fig 10.35 MO Diagram for O_2 molecule

Molecular orbital diagram of oxygen molecule (O_2)

Electronic configuration of O atom $1s^2 2s^2 2p^4$

Electronic configuration of O_2 molecule
$\sigma_{1s}^2, \sigma_{1s}^{*2}, \sigma_{2s}^2, \sigma_{2s}^{*2}, \sigma_{2p_x}^2 \pi_{2p_y}^2, \pi_{2p_z}^2, \pi_{2p_y}^{*1}, \pi_{2p_z}^{*1}$,

Bond order $= \dfrac{N_b - N_a}{2} = \dfrac{10-6}{2} = 2$

Molecule has two unpaired electrons hence it is paramagnetic.

Bonding in some Hetero nuclear di-atomic molecules
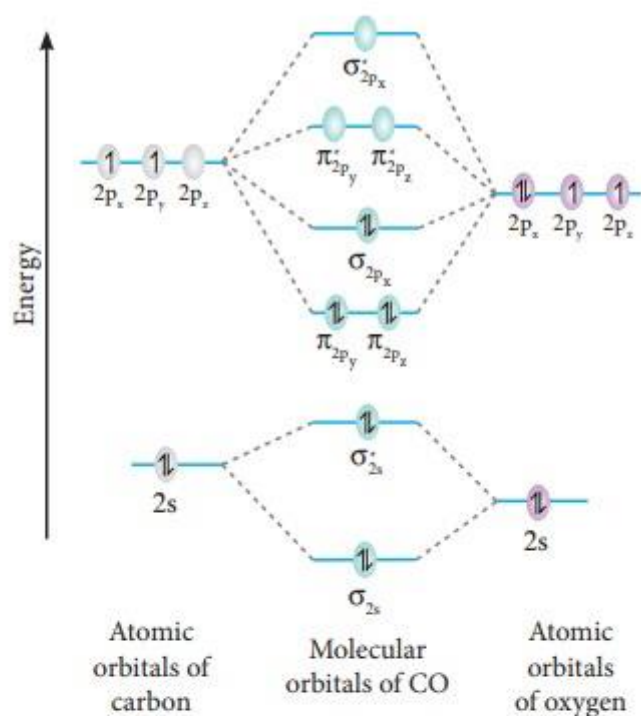
Fig 10.36 MO Diagram for CO molecule

Bonding in some heteronuclear di-atomic molecules

Molecular orbital diagram of Carbon monoxide molecule (CO)

Electronic configuration of C atom $1s^2\, 2s^2\, 2p^2$

Electronic configuration of O atom $1s^2\, 2s^2\, 2p^4$

Electronic configuration of CO molecule

$\sigma_{1s}^2, \sigma_{1s}^{*2}, \sigma_{2s}^2, \sigma_{2s}^{*2}, \pi_{2p_y}^2, \pi_{2p_z}^2, \sigma_{2p_x}^2$

Bond order $= \dfrac{N_b - N_a}{2} = \dfrac{10 - 4}{2} = 3$

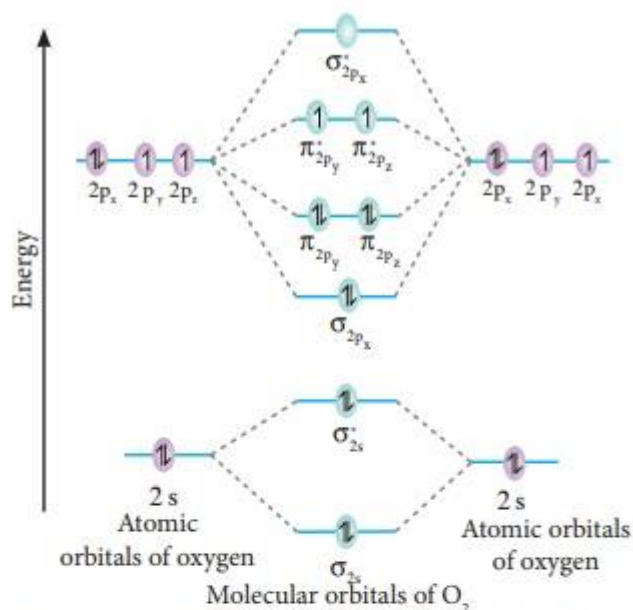Molecule has no unpaired electrons hence it is diamagnetic.
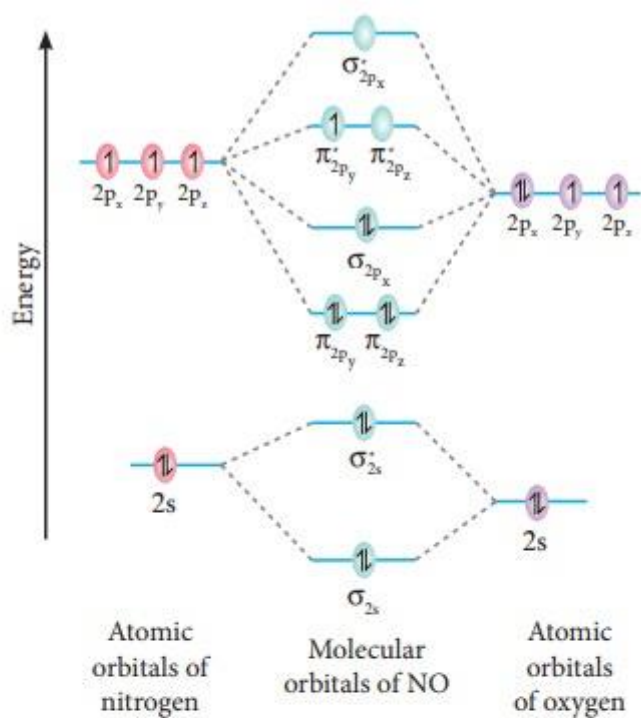
Fig 10.37 MO Diagram for NO molecule

Molecular orbital diagram of Nitric oxide molecule (NO)

Electronic configuration of N atom $1s^2\, 2s^2\, 2p^3$

Electronic configuration of CO molecule $\sigma_{1s}^2, \sigma_{1s}^{*2}, \sigma_{2s}^2, \sigma_{2s}^{*2}, \pi_{2p_y}^2, \pi_{2p_z}^2, \sigma_2 p_x^2\ \pi_{2p_y}^{*1}$

Bond order $= \dfrac{N_b - N_a}{2} = \dfrac{10 - 5}{2} = 2.5$

Molecule has one unpaired electron hence it is paramagnetic.

1.5.BAND THEORY OF SOLIDS

A solid contains an enormous number of atoms packed closely together. Each atom, when isolated, has a discrete set of electron energy levels 1s,2s,2p,....... If we imagine all the N atoms of the solid to be isolated from one another, they would have completely coinciding schemes of their energy levels.

If the atoms are brought in close proximity, the valence electrons of adjacent atoms interact. Hence the valence electrons constitute a single system of electrons common to the entire crystal with overlapping of their outermost electronic orbits. Therefore, the N electrons will now have to occupy different energy levels. This is brought about by the electric forces exerted in each electron by all the N nuclei. As a result of these forces, each atomic energy level is split up into a large number of closely spaced energy levels. A set of such closely spaced energy levels is called an energy band.

. For example, the 11 electrons in a neutral sodium atom, each occupy a specific energy level as shown:
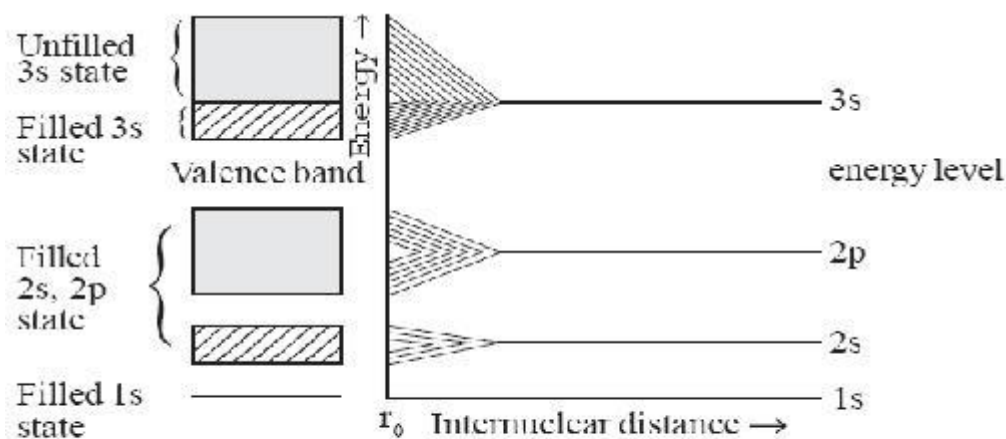
Fig. 10 Energy level of sodium

The energy levels of sodium become bands when the atoms are close together.

When the atoms are in solid, they interact with each other and the electrons have slightly different energies. The band formed from the atomic energy levels containing valance electrons is called valance band. These electrons have the highest energy. Above the valance band, there is the band of next higher permitted energies called the 'conduction band'. The conduction band corresponds to the first excited states; electrons can move freely in this band and are called 'conduction electrons'. The interval between conduction band and valence band in which electrons cannot occupy is called 'Forbidden gap.

Solids can be classified as metals, semiconductors or insulators based on conductivity or resistivity and energy bands:

- In case of metallic conductors, conduction band overlaps on the electrons in the valence band. E.g. sodium, magnesium etc.

- In insulators, there is a large gap between both these bands. Hence, the electrons in the valence band remain bound and no free electrons are available in the conduction band. e.g. Diamond, glass etc.

- Semiconductors have a small gap between both these bands. Some valence electrons gain energy from external sources and cross the gap between the valence and conduction bands. By this movement, they create a free electron in the conduction band and a vacant energy level in the valence band for other valence electrons to move. This creates the possibility of conduction.e.g. Silicon , Germanium etc.
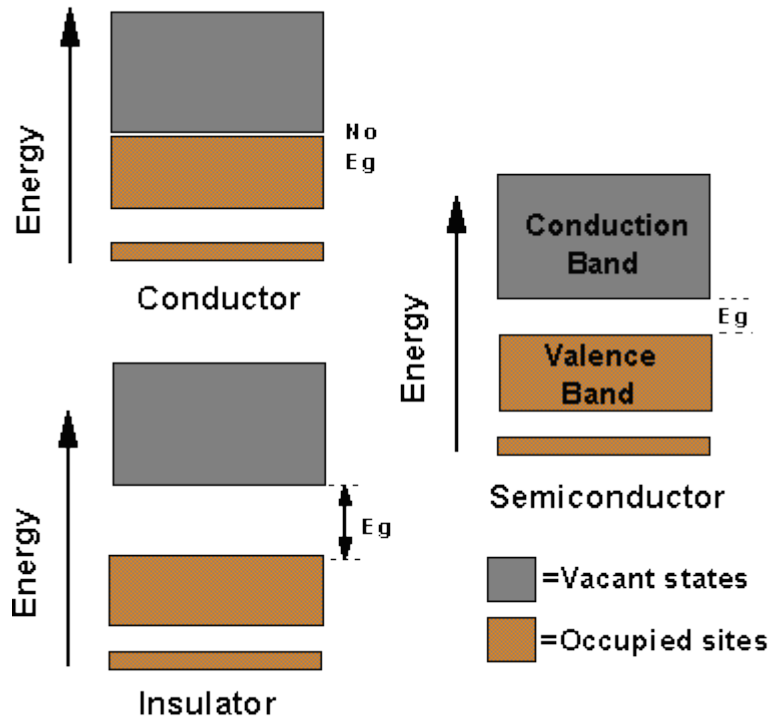
1.6. Imperfections or Defects in a Solid

In a crystalline solid, there is uniformity of their structure and arrangement of atoms. However, there are certain defects in this structure, that give solids certain characteristic features. .

This means that they have repeated arrangement of a unit cell to form a space lattice structure. So the arrangement of molecules, in the long run, will remain the same.

However, these crystals are not perfect. They have defects or imperfections in their arrangement of constituent particles. These defects are a deviation from their uniform arrangement of particles. The defects are of two kinds

Point Defects: When the deviation occurs around an ato m/particle it is a point defect. It could be due to displacement, an extra particle or a missing particle.

Line Defects: When there is an abnormality in the arrangement of an entire row, then it is a line defect.

- Point Defects

Point defects usually occur when the crystallization has occurred very rapidly, not allowing a perfect crystal arrangement to form. Although it should be noted there are imperfections in even during a slow crystallization. There are mainly three different kinds of point defects.

1.6.1 Stoichiometric Defects

Stoichiometric compounds are those who maintain their stoichiometry. That means they maintain their ratios of cations and anions as indicated by their chemical formula. The defects in the solid do not affect this ratio. They are of various kinds, such as

- Vacancy Defect

vacancy (missing atom)
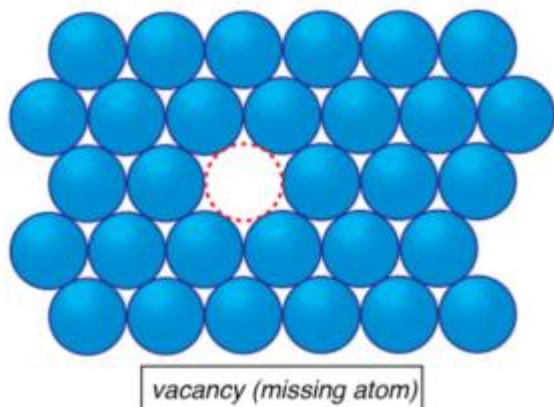
Here the lattice site is simply vacant, which means there is a missing particle. In a perfect crystal, there would not be this vacancy. This defect will lead to a reduced density of the solid. Some surrounding particle may move to fill in the gap, but the vacancy will only shift in the opposite direction, Also the solid structure of the crystal will ensure that the particles surrounding the vacant spot do not collapse.

- Interstitial Defect

There is an unoccupied space at the very center of the cube structure of the solid. When the eight spheres of a unit cell meet at the center they leave a little space, the interstitial site. Sometimes another particle will occupy this space. This is what we call an interstitial defect.

These are extra atoms or molecules or ions that occupy space which was supposed to be empty, which is why it is a defect. The density of the solid also increases due to such defects.

- Schottky Defects- In this defect, more than one particle is missing. But the number of cations missing is equal to the number of anions missing. So the electrical composition remains the same.

Since more than one particle is missing, the mass of the structure will decrease. But since the volume remains the same, the density of the solid will also decrease. If there are too many particles missing, then the lattice structure may be compromised. this could mean the stability of the structure may suffer. An example of this defect is NaCl, KCl, and other such ionic compounds

- Frenkel Defects

When a cation is missing from its normal position and has instead occupied an interstitial site it is a Frenkel Defect. Here the electrical neutrality will be unaffected. Also, it is usually cations that cause this defect since they can easily fit in the interstitial site due to their small and compact size.

Here no particles are actually missing, only the position is wrong. So the density of the solid will not change. It usually occurs in compounds where there is a significant size difference between cations and anions. Some examples are AgCl, AgBr etc.
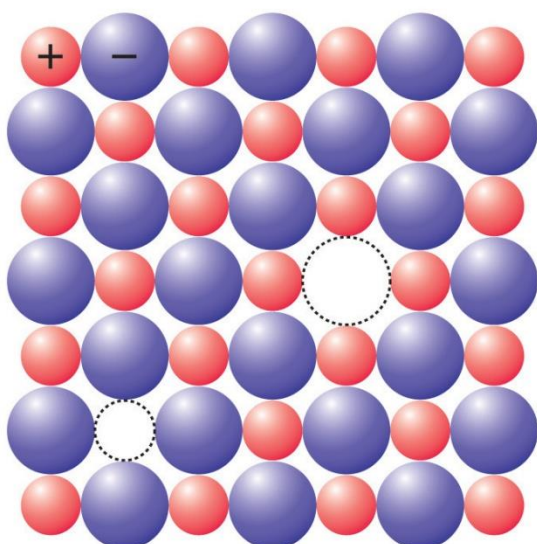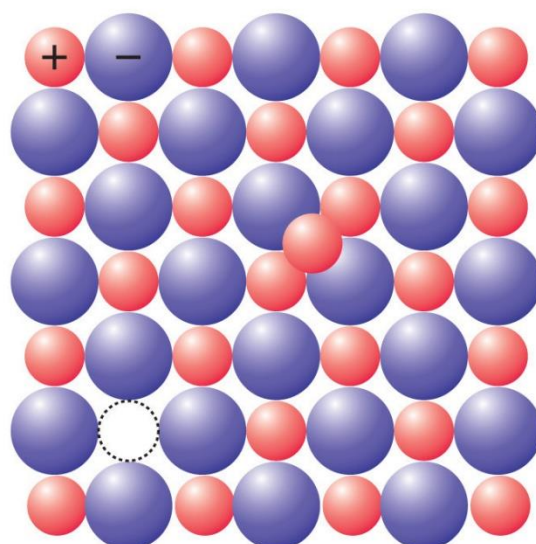
(a) Schottky defect   **(b) Frenkel defect**

Main points of difference between schottky and frankel defect

Schottky defect	Frenkel defect
1. It is due to equal no. of cations and anions missing from lattice sites. 2. It results in decrease in density of crystal 3. This is found in the highly ionic compounds with having cations and anions of same sizes NaCl, CaCl	1. It is due to missing of ions [usually cations] from the lattice sites and these occupies interstitial sites. 2. It has no defect on the density of crystal. 3. This is found in crystal with low coordination no. Example:- AgI, ZnS etc.

1.6.2 Non-Stoichiometric Defects

These defects will change the ration of ions in the solid. The number of cations and anions will not reflect as stated in their chemical formula. This imperfection is generally found in a large number of inorganic compounds. There are mainly two types of non-stoichiometry defects. If a result of the imperfactions in the crystal the ratio, of the cations and anions becomes difference from that indicated by ideal chemical formula. The defects are called non-stoichiometric defects.

- Metal Excess Defects

A negative ion may be missing from its lattice site, leaving a hole which is occupied by an electron, there by maintain the electrical neutrality.The interstitial sites containing the electron thus trapped in the anion vacancies are called the F – centers. They are responsible for imparting colour to the crystals.It is due to following factors:

- Anionic Vacancy: Sometimes an anion may be missing from its usual position in the unit cell. This empty space will be occupied by an electron to maintain the electric neutrality of the solid. This space that the electron invades, is known as the F-center. This F-center electron is what

gives the compound a color, One common example is NaCl and the yellow color it obtains on being heated.

- Extra Cations: On being heated many compounds result in having extra cations. These cations fit into the interstitial sites. To balance the neutrality an equal number of electrons do the same. But the ultimate result is the excess of metal in the solid. An example of this is when Zinc Oxide is heated and it losses oxygen.

- Metal deficiency Defects

In this defect, some cations are missing from the lattice site and for maintaining its electrical neutrality another remaining cation increase their valency. For example, FeO which is found with a composition of Fe 0.95 O. It may actually range from Fe0.93O to Fe0.96O.

In the crystal of FeO, some Fe^{2+} cations are missing and the loss of positive charge is made up by the presence of the required number of Fe^{+3} ions.

Metal Deficiency Defect
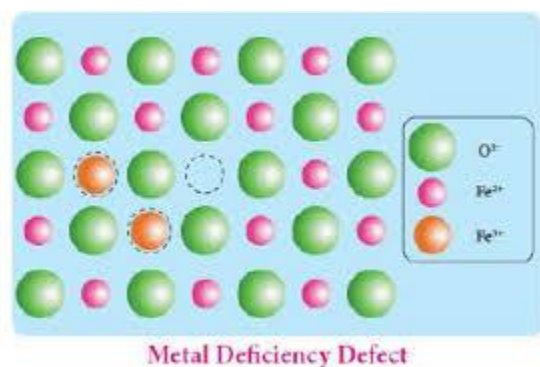
1.7. NANOMATERIALS

Nanomaterials are'material with any external dimension in the nanoscale (size range from approximately 1 – 100 nm) or having internal structure or surface structure in the nanoscale'.

Nanomaterials are of interest because at this scale unique optical, magnetic, electrical, and other properties emerge. These emergent properties have the potential for great impacts in electronics, medicine, and other fields. These emergent properties have the potential for great impacts in electronics, medicine, and other fields.Some nanomaterials occur naturally, but of particular interest are engineered nanomaterials (EN), which are designed for, and already being used in many commercial products and processes. They can be found in such things as sunscreens, cosmetics, sporting goods, stain-resistant clothing, tires, electronics, as well as many other everyday items, and are used in medicine for purposes of diagnosis, imaging and drug delivery.

The two main reasons why materials at the nano scale can have different properties are increased relative surface area and new quantum effects. Nanomaterials have a much greater surface area to volume ratio than their conventional forms, which can lead to greater chemical reactivity and affect their strength. Also at the nano scale, quantum effects can become much more important in determining the materials.

1.7.1 PREPARATION OF NANOMATERIALS:

When it comes to the synthesis of metallic Nanoparticles, two distinct approaches are utilized. The first is the top-down strategy and the second approach is referred to as the bottom-up strategy. While

the former deals with the reduction in size of current technological devices, the latter performs an opposite role, which is building of even more complex molecular devices on an atomic arrangement.

TOP-DOWN APPROACH

The top-down approach usually involves the following processes:

1. Cutting

2.Grinding

3.Itching.

4. Ionic/electronic irradiation

BOTTOM-UP APPROACH

The bottom-up approach utilizes physical and chemical processes that function at the nanoscale to integrate main components into bigger structures. A reduction in unit size, the approach yields a relevant consummation to the top-down approach. Biological systems provide a motivation for this approach in which natural forces of life harness their chemical counterparts to produce the structures.

Gold-palladium alloy nanoparticles which were based on carbon treated with acid and breaking down hydrogen peroxide are formed from the combination of white hydrogen and red oxygen when disallowing unwanted decay.

This approach has been used in the production of nanoparticles from condensation to coalescence of atomic vapors and liquids, respectively.

1. sol-gel techniques

This allows the production of nanomaterials from alkoxides or colloidal based solution. They take the form of monoliths, crystallized nano pigments, and thin layers. They are centered on reactions in polymerization. The three types of this are sol-gel, metal alkoxide, and pechini.

2.Lithgraphy in which growth of thin film is done.
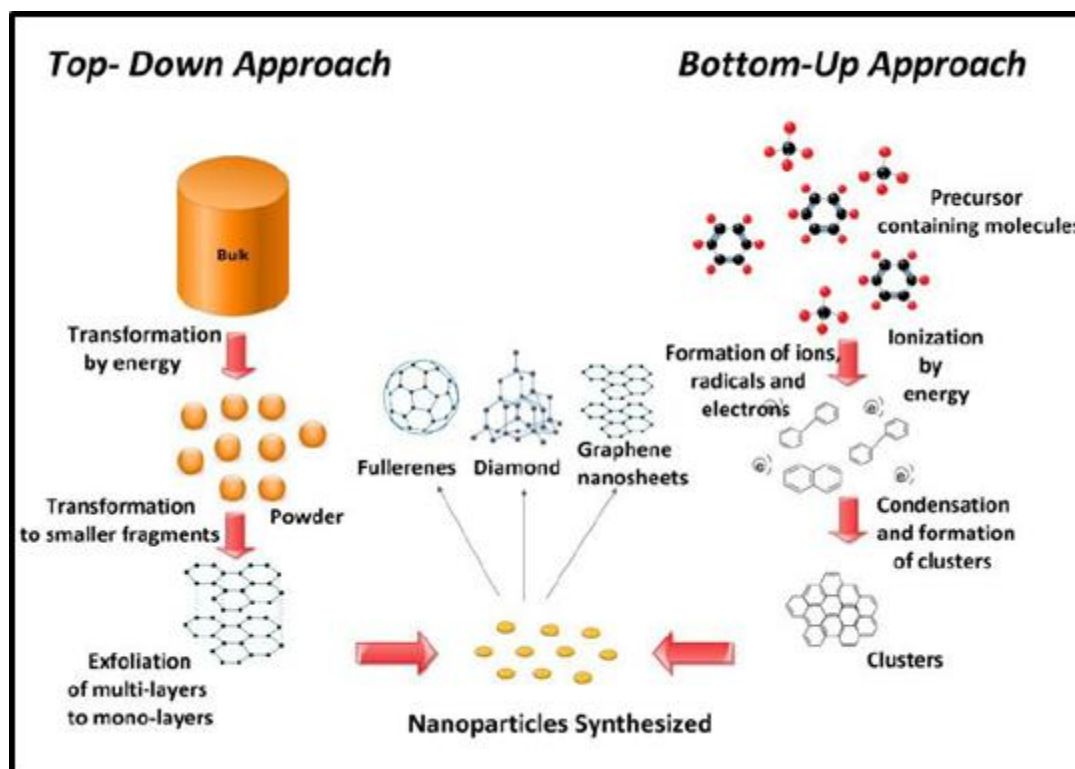
APPLICATIONS

Nanoscale additives to or surface treatments of fabrics can provide lightweight ballistic energy deflection in personal body armor, or can help them resist wrinkling, staining, and bacterial growth.

Clear nanoscale films on eyeglasses, computer and camera displays, windows, and other surfaces can make them water- and residue-repellent, antireflective, self-cleaning, resistant to ultraviolet or infrared light, antifog, antimicrobial, scratch-resistant, or electrically conductive.

Nanoscale materials are beginning to enable washable, durable "smart fabrics" equipped with flexible nanoscale sensors and electronics with capabilities for health monitoring, solar energy capture, and energy harvesting through movement.

Nanoparticles are used increasingly in catalysis to boost chemical reactions. This reduces the quantity of catalytic materials necessary to produce desired results, saving money and reducing pollutants. Two big applications are in petroleum refining and in automotive catalytic converters.

Nano-engineered materials make superior household products such as degreasers and stain removers; environmental sensors, air purifiers, and filters; antibacterial cleansers; and specialized paints and sealing products, such a self-cleaning house paints that resist dirt and marks.

Nanoscale materials are also being incorporated into a variety of personal care products to improve performance. Nanoscale titanium dioxide and zinc oxide have been used for years in sunscreen to provide protection from the sun while appearing invisible on the skin.

1.8.GRAPHITE

- Graphite is one of the allotrope of carbon .

- Graphite is an allotrope of carbon in which each carbon atom is sp2 hybridized and forms covalent bonds with three other sp2 hybridised carbon atoms. This results in formation of interlinked six membered rings.

- π bonds are formed between carbon atoms by utilizing half filled unhybridised 2pz orbital on each carbon atom..

- It is the only non metal which is a good conductor of heat and electricity.

Structure

This element is crystalline in nature; however, perfect crystals of graphite are rarely found. The carbon atoms in its structure are arranged in a hexagonal manner in a planar, condensed ring system. This gives the graphite crystals a hexagonal shape. Different layers of this element are stacked together and held by weak covalent forces to form a giant covalent structure.

- This crystal carbon has a structure that is planar and layered.

- Every layer has atoms of carbon arranged in a honeycomb-like a network with the division of 0.142 nm with 0.335 nm distance between planes.

- There is a covalent bonding for atoms in the plane with the criteria being met by only three out of four probable bonding sites

- The graphite would be conducive electrically owing to the fourth electron having a chance to migrate into the plane.

- The layers of the carbon crystal could swiftly move past each other as the layers could be separated easily as van der Waals bonds that are weak-hold them together.

- The widely-known types of this carbon crystal viz. beta and alpha have almost the same material properties with the exception of the layers of graphene stack a little differently. The alpha crystal would seem bent or as flat. To convert one form to other viz. from alpha to beta it could be done by treating it mechanically. Then from beta to alpha conversion would be done by heating the crystal above 1300 °C.

Layer Structure of Graphite
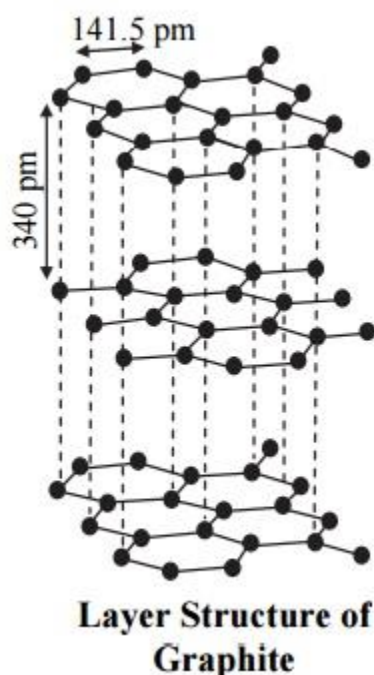
Chemical Properties

- Graphite is chemically inert to almost all chemicals.

- On applying pressure on graphite, its layers start to slide over one another. Therefore graphite is soapy to touch.

- The melting point of graphite is high.

- In graphite, three electrons are involved in sigma bonding and the fourth electron is free to move on applying potential difference, so it is good conductor of electricity.

Uses of Graphite

- Graphite can be used in the manufacture of 'lead' used in pencils.

- It is also used in refractories and steel making.

- Due to soapy nature, it is used asLubricant.

- Graphite is used in making electrodes and molds in foundry.

1.9.FULLERENES

- Fullerenes are molecules (pure substances made of only one type of atom) of carbon that can take on different shapes like tubes, spheres, cubes, etc. One thing that characterizes fullerenes is they have a hollow core, or empty region of space inside the molecule. It's made up of only carbon, and there is always a hollow space inside the structure.

- In 1990 physicists W. Krätschmer and D.R. Huffman for the first time produced isolable quantities of C60 by causing an arc between two graphite rods to burn in a helium atmosphere and extracting the carbon condensate so formed using an organic solvent.

- Fullerene, also called buckminsterfullerene, any of a series of hollow carbon molecules that form either a closed cage ("buckyballs") or a cylinder (carbon "nanotubes").

- The C60 molecule was named buckminsterfullerene (or, more simply, the buckyball) after the American architect R. Buckminster Fuller, whose geodesic dome is constructed on the same structural principles. The elongated cousins of buckyballs, carbon nanotubes, were identified in 1991 by Iijima Sumio of Japan.

    Preparation:

- Fullerenes are made by heating of graphite in an electric are in the presence of inert gases such as helium or argan. The sooty material formed by condensation of vaporised C" small molecules consists of mainly C60 with a smaller quantity of C70 and traces of other similar fullerenes C32, C50, C76 and C84. Thus fullerenes can be easily extracted from the soot by dissolving in benzene or hydrocarbon solvents, giving a wine-red solution and finally mustard coloured crystals. The different fullerenes are separated by chromatography. Out of all the fullerenes, C60 isotope is the most stable.

- Structure:

- Follerenes are cage like molecules composed of 60 carbon atoms (C60) joined together by single and double bonds to form a hollow sphere with 12 pentagonal and 20 hexagonal faces—a design that resembles a football, or soccer ball. A six-membered ring is fused with six or five-membered rings but a five membered ring can only fuse with six-membered rings..

- In this structure, each carbon atom forms three sigma bonds with other three carbon atoms. The remaining electron at each carbon is delocalised in molecular orbital, which in turn gives aromatic character to the molecule.
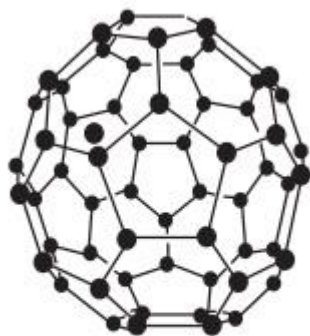
The Structure of C$_{60}$, Buckminster-Fullerene

f.

PROPERTIES OF FULLERENE:

• It is mustard coloured solid, which appears brown to black with increasing thickness of its film.

• On sublimation, it forms translucent magenta face-centered cubic crystals.

• It is moderately soluble in aromatic hydrocarbons giving magenta solution.

• As a pure solid, it is electrically insulating. With proper impurity addition , it can be made highly conductive and super conductive.

USES OF FULLERENE:

• It is used for the preparation of electronic and microelectronic devices.

• It is used for the preparation of non-linear optical devices.

• It is used for the preparation of batteries as charge carriers.

• It is used for the preparation of super conductors.

• It is used for the preparation of soft ferromagnet with zero remanence.

1.10 LIQUID CRYSTALS

 Liquid crystals form a state of matter intermediate between the solid and the liquid. For this reason, they are referred to as intermediate phases or mesophases.

When molecular crystals are heated to their melting point, they usually change directly into the liquid state. The periodic structure of die lattice as well as the orientational ordering of the molecules is destroyed simultaneously. However, if the constituent molecules have a pronounced anisotropy of shape, such as rod or disc, the melting of the lattice may precede the disappearance of the orientational ordering leading an intermediate phase composed of molecules which are more or less parallel to each other but at the same time exhibiting a certain degree of fluidity. The molecules can slide over one another while still preserving their parallelism. The fluid is therefore anisotropic; it is turbid and, like a crystal, shows optical birefringence and dielectric anisotropy. At a higher temperature, there is orientational melting and the anisotropic fluid transforms into the ordinary isotropic clear liquid. Such intermediate (or meso) phases are referred to as liquid crystals (LCs). They combine both, order and mobility.
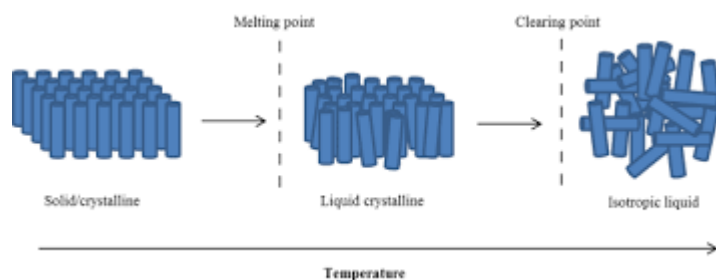
Classification of liquid crystals

Liquid crystals can be roughly divided into two areas:

1. Thermotropic, whose mesophase formation is temperature dependent,

2. Lyotropic, whose mesophase formation is solvent and concentration dependent

The Lyotropic liquid crystal can be classified as:

(a) Nematic liquid crystal

(b) Smectic liquid crystal

(c) Cholesteric liquid crystal

(**a**) **Nematic liquid crystal:**

The nematic phase of calamitic liquid crystals is the simplest liquid crystal phase. The name "nematic" comes from the Greek word, nema means thread-like which can be observed under polarizing microscope. This name was given due to the thread-like discontinuities produced by variations in the molecular organization. The nematic phase is essentially a one dimensionally ordered elastic fluid in which the molecules have a high degree of long range orientational order, but there is no long range translational order (positional order) It is the least viscous and least ordered mesophase with a high degree of fluidity. The phase is usually very easy to identify by optical polarizing microscope. In the nematic phase, the constituent molecules are completely disordered with respect to each other but the long molecular axes statistically point in a preferred direction known as the director (q). The most common texture adopted by the nematic phase is schileren.

(b) Smectic liquid crystal:

Smectic liquid crystals dif'fer from nematics as smectics have two degrees of order namely orientational and positional. In smectic mesophase, the molecules form layers and translation of molecules from one layer to another is limited. Within these layered systems, a variety of molecular arrangements is possible leading to different sub phases . The term smectic comes from the world smectos-soap like, as the basic layered structure in the smectic phase gives them a soapy feel . The smectic phase is characterized by a long range orientational order and positional order which gives layered structure. The inter layer attractions are weak when compared with the lateral forces between the molecules and the layers are able to slide freely over one another. As a result, the smectic phase has fluidity and is more viscous than nematic phase. The smectic phase is more ordered than the nematic phase. The smectic phase exhibits polymorphism and the lamellar nature of smectic phase allows various combinations of molecular correlations both within the 'layers' and between the 'layers' each of which consists of different type of smectic phase . The smectic phases are found at lower temperatures than nematics which can be identified under optical polarising microscope.

(c) Cholesteric liquid crystal

The cholesteric phase is also called chiral nematic phase or twisted nematic phase . Cholesteric phase was first discovered in cholesterols. 'I'he chiral nematic phase exhibits chirality and is associated with the presence of an asymmetric carbon atom. so that left and right hand versions of molecules cannot be commuted by simple reorientation. The molecules forming this phase are always optically active. i. e. they have distinct right- and left-handed forms. Only chiral molecules (i.e., those that lack of inversion symmetry) can give rise to such a phase. This phase exhibits a twisting of the molecules perpendicular to the director, with the molecular axis parallel to the director.

Nematic phase   Smectic phase   Cholesteric phase

Increasing opacity
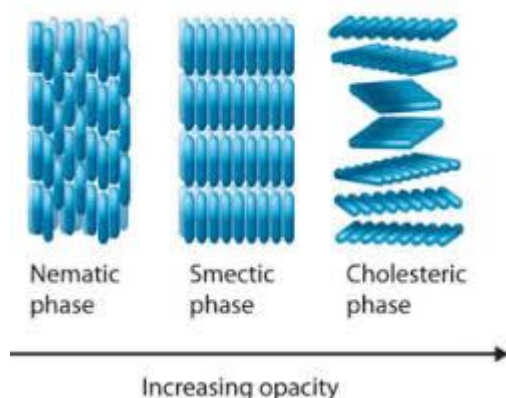
APPLICATIONS

- The most important use of liquid crystals is in displays because the molecules of a liquid crystal can control the amount, color, and direction of vibration of the light that passes through them.
- They are used in the LCDs and in digital watches.
- Also used in handheld calculators; flat-screen monitors; and car, ship, and aircraft instrumentation.
- They are used in all kinds of display devices including computer monitors and laptop screens, TVs, clocks, visors, and navigation systems.

PREVIOUS YEARS UNIVERSITY QUESTIONS

1. Boiling point of water (H2O) is higher than that of Hydrogen Fluoride (HF) explain why?
2. Define Bond Order. Give its significance.
3. O_2 is paramagnetic while N_2 is diamagnetic. Explain with the help of MOT.
4. Define intra moiecular hydrogen bonding. Give example.
5. Draw the Molecular Orbital diagram of NO and O_2. Calculate its bond order and predict the magnetic behavior.
6. Why He_2 does not exist in environment?
7. What do you understand by a metallic bond ? Discuss it on the basis of nolecular orbital theory.
8. Discuss stiochiometric defects in ionic solid.
9. What is Schottky defect? Give examples.
10. Define frenkel defect with example.
11. What is Crystal imperfection? Explain the zero dimensional imperfection in solid.
12. What are stoichiometric and non-stoichiometric defects? Explain Frenkel and Schotky defects found in solids.
13. Describe the preparation, structure and applications of fullerenes.

14. Why does graphite show conduction property?
15. Discuss the structure ,properties and applications of graphite.
16. Explain the preparation, properties and applications of an allotrope of Carbon having truncated icosahedron geometry.
17. What are the fullerenes.discuss their properties and applications.
18. With the neat labeled diagram, explain the conductivity and lubricating properties of Graphite.
19. What do you understand by Mesomorphic state? Classify them on the basis of temperature and mention three important applications of it.
20. What are Liquid crystals? Classify them on the basis of temperature and mention four important applications of it.
21. What are nanomaterials. Discuss its preparation and important applications.

VIDEO LINKS:

1 https://www.youtube.com/watch?v=FMxuss0RXOU

2.https://www.youtube.com/watch?v=IcAdSETGUtg

3.https://www.youtube.com/watch?v=kGJIVYO3nf4

4. https://www.khanacademy.org/science/in-in-class-12th-physics-india/in-in-semiconductors/in-in-band-theory-of-solids/v/band-theory-of-solids-class-12-india-physics-khan-academy

 5.https://www.youtube.com/watch?v=utanySlCBFE

6. https://www.youtube.com/watch?v=MuWDwVHVLio

7. https://www.youtube.com/watch?v=ckUJLjXa8aY

8. https://www.youtube.com/watch?v=1xWBPZnEJk8

9. https://www.youtube.com/watch?v=ie-KfQionjY