CHEMICAL BONDING

UNIT-1

1. **Ionic Bond**– The bond formed by the complete transfer of one or more electrons from one atom to another atom is known as ionic or Electrovalent bond. In this type of bond, one of two combining atoms should be electropositive whereas the other should be electronegative.

   The compounds formed through electrovalency are known as electrovalent compounds.

**Characteristics of Electrovalent Compounds**

1. These compounds contain charged atoms called ions which are held together by electrostatic force of attraction. The ions are arranged in regular way in a crystal lattice.

   They are generally soluble in polar solvents like H$_2$O, liquid NH$_3$ but insoluble in the non-polar solvents like benzene, CCl$_4$ etc.

2. These compounds when melted or dissolved in a polar solvent, conduct electricity and ions are liberated on the oppositely charged electrodes.

3. They have sufficiently high melting & boiling points. This is because of high electrostatic force of attraction between the oppositely charged ions.

4. Because of non-directional nature of bond they do not show isomerism.

**Covalent Bond**
Kossel’s theory of electrovalency could not explain the combination between the atoms of almost similar electro negativity such as H₂, Cl₂ etc. The combination of atoms in such compounds was explained by the concept of covalency given by Lewis. 1916.

The bond formed between atoms by mutual shairing of electrons in known as covalent bond.

**Characteristics of covalent Compounds**

1. These compounds are generally gases or liquids at ordinary temperature. They are solid only when their molecular weights are high.
2. They are insoluble in polar solvents like H₂O but are soluble in non-polar solvents like benzene, CCl₄ etc.
3. They do not conduct electricity because they are not ionized in solution or in the fused state.
4. They have generally low melting & bonding points.
5. They undergo molecular reactions therefore, slow as compared to ionic reactions.
6. Since the co-valent bond is rigid and directional, these compounds show space isomerism.

**Co-ordinate Bond** :-

The way of chemical combination of two atoms involving sharing a pair of electrons which are contributed by only one of combining atoms is known as co-ordinate valency and the resulting bond is known as co-ordinate bond.

The atom which provides the electron pair for shairing is known as donar atom, whereas the atom which receives is known as acceptor. The bond is represented by an arrow head (→) pointing away from donar to the acceptor atom.

**Characteristics of Co-ordinate compounds**

1. They do not conduct electricity as they are not ionized in solution or fused state.
2. They are generally insoluble in polar solvent but are soluble in nonpolar solvent.
3. These compounds have melting and boiling points higher than that of the covalent compound but lower than electrovalent compound because of semi polar nature of bond.
4. Since the co-ordinate bond is also rigid & directional, these compounds show isomerism.

**Polar and Non-Polar Co-valent Bond**

A Co-valent bond formed between two identical or similar atom is said to be a non-polar covalent bond but if formed between two dissimilar atoms, the bond formed is said to be a polar covalent bond. In the non-polar covalent bond the shared pair of electron is equally attracted by both atoms and lies exactly midway between them as in hydrogen molecule H :H.

In the case of a covalent bond formed between two dissimilar atoms, one of the atoms generally has greater tendency to attract the electrons towards itself. The electron pair is therefore, pulled closer to that atom, as in HF molecule.

This un-symmetric distribution of electrons leads to charge separation i.e. development of partial negative charge near fluorine end and partial positive charge near H end.

The molecules formed are said to be polar molecules.

**Hydrogen Bonding**

Whey hydrogen is co-valently bonded to a highly electronegative elements such as F, O, & N the hydrogen atom forms a weak bond with another highly electronegative atom. This weak bond is called hydrogen bond and is represented bas

Where X and Y are highly electronegative atoms like N, O & F. The dotted line represents hydrogen bond and the solid line represents the original co-valent bond in the molecule.
The cause of formation of hydrogen in compounds of with strongly electronegative elements (F, O or N) the shared pair of electrons lies for away from hydrogen atom. Thus the hydrogen atom acquires a small positive charge which attract the other electronegative atom of neighbouring molecule.

**Types of hydrogen Bonding**

Hydrogen bonding may be classified into two types :-

1. **Intermolecular Hydrogen Bonding**
   
   This type of bonding involves electrostatic force of attraction between hydrogen and on electronegative atom of two different molecules of the same or sometimes different substances e.g.

2. **Intramolecular Hydrogen Bonding**
   
   This type of bonding involves electrostatic force of attraction between hydrogen and an electronegative atom of the same molecule.

**Effect of Hydrogen Bonding**

1. Melting and Boiling Points – The compounds having intermolecular hydrogen bonding have comparatively high melting and boiling point. This is the reason why HF is liquid whereas HCl, HBr and HI are gases at ordinary conditions.

2. Solubility :- Organic compounds are generally insoluble in water put the organic compounds capable of forming hydrogen bonds with water (such as alcohol, acid etc.) are soluble in water.

**Theories of Co-valent Bonding**

According to Lewis concept, a covalent bond is formed by the mutual sharing of electrons between two atoms. This concept could not explain the nature of forces which hold two atoms together in a covalent molecule. In order to explain these forces, Heitler& London in 1927 put forward valence Bond theory which was later extended by Pauling Slater in 1931.
**Valence Bond Theory**

Heitler and London calculated the energy of two interacting hydrogen atoms when they are brought from large distances to form a hydrogen molecule. The energy curves so obtained may be represented as –

The spin of the electrons of two hydrogen atoms may be in same direction or in the opposite directions. When two hydrogen atoms having similar spins of their electrons are brought near to one another, the potential energy of the system increases as shown curve I. This is due to strong repulsive forces between the electrons of similar spins. When two hydrogen atoms having opposite spins of their electrons the potential energy of the system decreases as in curve II. As the distance between two atoms decreases, there occurs an increasing in the force of attraction & ultimately at a particular internuclear distance the potential energy of the system is minimum. On further decrease in internuclear distance, the potential energy of the system increases. The distance at which the potential energy of the system is minimum shows bond formation.

**Molecular Orbital Theory**

This theory was proposed by Hund and Mulliken in 1932. According to this theory, the atomic orbitals combine to form the molecular orbital in which the identity of both atomic orbitals is lost. All the electrons belonging to both atoms move along the entire belonging to both atoms move along the entire molecule under the influence of all the nuclei.

As atomic orbitals can be expressed in terms of wave function obtained from the solutions of Schrodinger wave equations, similarly wave equation can be written for whole molecules. For this an approximate method known as Linera Combination of Atomic Orbitals (LCAO) is used.

**LCAO Method**
According to this method, the molecular orbitals are formed by the linear combination (addition or subtraction) of atomic orbitals of combining atoms. Suppose A and B are two hydrogen atoms and $\psi_A$ and $\psi_B$ are the wave functions of the electrons of atoms A and B respectively. When these two hydrogen atoms combine to form molecular orbitals, the linear combination of atomic orbitals takes place by addition or subtraction of wave function of AO's to give two molecular orbitals (MO's)

1. Mo$_s$ obtained by addition of wave functions of AO's is called Bonding Molecular orbitals (BMO) and is represented by $\psi_{AB}$

$$\psi_{AB} = \psi_A + \psi_B \quad \ldots \ldots \quad (1)$$

2. Mo$_s$ obtained by addition of wave functions of AO's is called Antibonding Molecular orbital (ABMO) and is represented by $\psi_{AB}^*$

$$\psi_{AB}^* = \psi_A - \psi_B \quad \ldots \ldots \quad (2)$$

We know that the square of the wave function ($\psi^2$) is known as probability of finding electron in particular orbital, therefore

$$\psi_{AB}^2 = (\psi_A + \psi_B)^2 = \psi_A^2 + \psi_B^2 + 2\psi_A\psi_B \quad \ldots \ldots \quad (3)$$

$$\psi_{AB}^* = (\psi_A + \psi_B)^2 = \psi_A^2 + \psi_B^2 - 2\psi_A\psi_B \quad \ldots \ldots \quad (4)$$

From equation (3) & (4) we can say that the probability of finding the electrons in BMO is greater than either of atomic orbitals ($\psi_A + \psi_B$) by a factor of $2\psi_A\psi_B$. Whereas in ABMO the finding of their parent atomic orbitals ($\psi_A + \psi_B$) by the factor $2\psi_A\psi_B$.

In the case of BMO the attraction of both the nuclei for both the electrons is increased resulting in lowering of energy, while in ABMO electrons try to go away from nuclei resulting in higher energy.
**Energy level Diagram for Molecular Orbitals**

The energy levels of the molecular orbitals have been determined experimentally by spectroscopic method and these follow the order :-

However the experimental evidences shows that the above order is not correct for all the molecules. In second row molecules such as B₂, C₂, N₂ the \( \sigma \) 2px MO is higher in energy than \( \pi \) 2py. MOs. The order of MOs for these molecules is :-

Thus the molecular orbital diagram fro molecules Li₂, Be₂, B₂, C₂, N₂ is as follows

For the molecules O₂, F₂, Ne₂ molecular orbital diagram is as follows :

**Bond Order**

Bond order in a molecule is one half of the difference between number of electrons is BMOs and the number of electrons is ABMOs.

\[
\text{Bond Order} = \frac{N_b - N_a}{2}
\]

Where \( N_b \) = No. of electrons in bonding molecular orbital  
\( N_a \) = No. of electrons in anti bonding molecular orbital  

The bond order determined by above formula gives up following information :-

a) A molecule/ion is stable if \( N_b > N_a \).

b) Greater the bond order greater is the bond dissociation energy therefore greater the stability of the molecule.

c) Bond length is inversely proportional to the bond order i.e. greater the bond order smaller the bond length.

d) The existence of molecule/ion is not possible if bond order is zero.

The molecules or ions having unpaired electron in any molecular orbital are paramagnetic, whereas those have paired electron in all molecular orbitals are diamagnetic.
Metallic Bond

“The force that bind metals atoms of a metal together is called metallic bond.” Metallic bond results from a delocalization of valence-orbital electron between neighbouring atoms. Thus the metallic crystal consists of positive ions called kernels, permeated by cloud of valence electrons called electron gases.

Metals are characterized by properties such as good thermal and electrical conductivity, a bright appearance called metallic luster, high malleability, ductility and tensile strength.

There are three major theories to explain bonding in metals.

1) **Free electrons theory** – According to this theory each atom in a metal crystal losses all its valency electrons due to low ionization energy of the metal atoms. The metal is regarded as a group of positive metal ions which are held together in a regular geometrical pattern by this electron pool or gas. The force that binds a metal ion into the mobile electrons within the sphere of influence in known as metallic bond.

2) **Valence Bond Theory** – According to this theory, metallic bond is essentially covalent in origin and metallic structure involves resonance of electron pair bonds between each atom and its neighbor. For example Lithium atom with 2s^{1} i.e. one electrons in its outermost shell, may be shared with one of the neighbours forming a normal two electron bond.

\[
\begin{align*}
\text{Li} & \quad \text{Li} - \text{Li} & \quad \text{Li} & \quad \text{Li-Li} & \quad \text{Li-Li} \\
\text{Li} & \quad \text{Li-Li} & \quad \text{Li} & \quad \text{Li-Li} & \quad \text{Li-Li}
\end{align*}
\]

There are some more resonating structures of Li which account for large resonance energy and hence large cohesive force.

\[
\begin{align*}
\text{Li-Li} & \quad \text{Li-Li} & \quad \text{Li} & \quad \text{Li-Li-Li} \\
\text{Li-Li} & \quad \text{Li Li} & \quad \text{Li} & \quad \text{Li-Li-Li}
\end{align*}
\]

Molecular orbital or Band theory
This is the most acceptable theory for metallic bond. Band theory is based on the delocalization of free electrons in all the atoms of metal. Since two atoms combine to form a diatomic molecule the number of molecular orbitals is equal to the number of atomic orbitals. Let us consider the formation of sodium metal by adding Na-atoms one at a time forming Na$_2$, then Na$_3$, Na$_4$, Na$_5$ and so on until the formation of Na$_n$. In diatomic Na$_2$ molecule two 3s orbital combine to form two molecular orbitals $\sigma$ 3s. In Na$_3$ molecule the three 3s orbitals overlap to form three molecule the three 3s orbitals overlap to form three molecular orbitals one bonding one antibonding and one non-bonding molecular orbital. In the formation of NaN, n-atomic orbitals overlap to form n number of molecular orbitals, half of which are bonding and the other half are anti-bonding molecular orbitals. As the number of atoms increases, the spacing between the energy of various molecular orbitals decreases. The molecular orbitals are so closed that a band of orbitals are formed. The band containing outer electron or valence electron is called valence band. Since 3s and 3p orbitals do not much differ in energy the band of molecular orbitals formed from the s-orbitals and p-orbitals join continuously this is called conduction band. Conduction band may be either partly filled or vacant. Electrons in lower filled levels of the valence band can easily migrate to the vacant orbitals of the conduction band. On the basis of molecular orbital theory the conduction property of metals can be explained.

**Conductor**

In conductor there is no energy gap between valence band and conduction band and conduction band and electrons can easily move in any molecular orbitals.

**Insulator**
In insulator there is large gap between valence band and conduction band called forbidden gap. The electrons are not free to move in outer vacant molecular orbitals i.e. conduction band.

**Semi conductor**
If the energy gap or forbidden gap between valence band & conduction band is larger than conductor but smaller than in insulator, the substance is said to be semiconductor.

**SOLID STATE**
Solids are the substances characterized by definite shape, volume, non-compressibility, rigidity and mechanical strength. The atoms molecules or ions in solids are closed packed and they are held together by strong forces. Solid may be classified as either crystalline or amorphous.

**Crystalline Solids**: A substance whose constituents are arranged in an ordered manner in a definite geometrical form is called crystalline solid. e.g. Nacl, diamond etc.

**Properties of Crystalline Solids**

a) A crystalline solid has a finite and regular geometry due to definite arrangement of atoms, molecules or ions in three dimensional space.

b) Crystalline solid has sharp melting point.

c) When subjected to mechanical stress a crystal tend to fracture along a perfectly definite direction.

d) A crystalline solid is anisotropic i.e. its physical properties like mechanical, electrical and optical properties are difference in different directions.

**Amorphous Solids**
The solids which do not have any definite geometrical shape are called amorphous solids. e.g. glass, rubber, plastics etc.

**Properties of Amorphous solids**
a) Amorphous solids are considered as super cooled liquid and there is no regularity in structure.

b) Amorphous solids do not have sharp melting point. On increasing temperature, the viscosity of amorphous substances decreases and gradually changes into the liquid state.

c) They are isotropic i.e. the physical properties like mechanical, thermal, electrical and optical properties are same in all directions.

**Coordination Number**

Ionic solids are held together by the electrostatic force of attraction between positive & negative ions. In general there will be repulsion between ions of same charge are adjacent. Attraction will occur when a positive ion is surrounded by negative ions and vice-versa. The attraction force will be maximum when each ion is surrounded by greatest possible number of oppositely charged ions. The number of ions surrounding any particular ion is called the co-ordination number.

**Radius Ratio Rule**

In ionic solids the co-ordination no. as well as geometric shape of crystals depends very largely on relative sizes of the ions i.e. on the radius ration

\[
\text{Radius Ratio} = \frac{r_+}{r_-}
\]

\( r_+ \) size of positive ion, \( r_- \) = size of negative ion

If the co-ordination number of an ionic AX is three then there X- ions are in contact with one A+ ion as in fig. I. A limiting case arises when the X- ions are also in contact with one another as in fig. II. By simple geometry this gives the radius ratio 0.155. This is the lower limit for a co-ordination number three. If the radius ratio is less than 0.155 then the positive ion is not in contact with the negative ions and the structure will be unstable. As the radius ratio increases above 0.225 it
becomes possible to fit four ions around one and so on for 6 & 8 ions round one. The co-ordination number & the limiting radius ratio can be worked out by simple geometry and are given below –

<table>
<thead>
<tr>
<th>Limiting Radius Ratio</th>
<th>Co-ordination No.</th>
<th>Geometrical Shape</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;0.155</td>
<td>2</td>
<td>Linear</td>
</tr>
<tr>
<td>0.155-0.225</td>
<td>3</td>
<td>Trigonal</td>
</tr>
<tr>
<td>0.225-0.414</td>
<td>4</td>
<td>Tetrahedral</td>
</tr>
<tr>
<td>0.414-0.732</td>
<td>6</td>
<td>Octahedral</td>
</tr>
<tr>
<td>0.732-0.999</td>
<td>8</td>
<td>Body Centered cubic</td>
</tr>
</tbody>
</table>

Thus if the ionic radii are known the radius ratio can be calculated hence the co-ordination no. and shape may be predicted.

**Calculation of Limiting Radius Ratio**

**Radius Ratio for Co-ordination No. 3**

A trigonal site is formed when the anions surrounds one cation. If \( r_+ \) and \( r_- \) are the radii of cations and anions respectively then from trigonal AOE

\[
\cos 30^\circ = \frac{AE}{AO}
\]

\[
\cos 30^\circ = \frac{r_-}{r_+ + r_-}
\]

\[
\frac{r_+ + r_-}{r_-} = \frac{1}{\cos 30^\circ}
\]

\[
\frac{r_-}{r_-} + 1 = 1.155
\]
Radius Ratio for Co-ordination No. 4
A tetrahedral site is formed when four anions surrounds one cation. If \( r_+ \) and \( r_- \) are the radii of cations and anions respectively. then from triangle AOC

In triangle AOC

\[
\angle AOC = \frac{109^028''}{2} = 54^044'
\]

\[
54^044' = \frac{AC}{AO}
\]

\[
\sin 54^044' = \frac{r_-}{r_+ + r_-}
\]

\[
\frac{r_+ + r_-}{r_-} = \frac{1}{\sin 54^044'}
\]

\[
\frac{r_+}{r_-} = 0.225
\]

Radius ratio for co-ordination No. 6
A octanedral site is formed when six anions surrounds are cation.

from \( \Delta AOE \)

\[
\cos 45^0 = \frac{AE}{AO}
\]

\[
\cos 45^0 = \frac{r_-}{r_+ + r_-}
\]

\[
\frac{r_+ + r_-}{r_-} = \frac{1}{\cos 45^0}
\]

\[
\frac{r_+}{r_-} + 1 = 1.414
\]

\[
\frac{r_+}{r_-} = 0.414
\]
Unit Cell

Unit cell is defined as the smallest geometrical portion of crystal, which repeated in three dimensional space, generate the complete crystal.” OR “Unit Cell is an arrangement of atoms, molecules or ions at definite distances and angles in three dimensional space which is repeated throughout the crystal”.

There are three types cubic unit cells.

1. Simple cubic Unit cell : The unit cell in which the lattice points are present at its corners. It is also called primitive or basic unit cell.

2. Face central cubic unit cell (fα) :- The unit cell in which the lattice points are present at its corners as well as at the centres of each face.

3. Body central cubic unit cell (bcc) :- The unit cell in which the lattice points are present at its corner as well as at the centre of the cubic body.

Calculation of number of atoms of an element in cubic unit cells:

1) **Simple cubic Unit cell** :- In this type of unit cell, there is one atom at the corner of the cube. Since each corner atom is shared by eight unit cells equally. So each corner contribute 1/8 atom to each unit cell. Since there are eight corners in cube

Number of atom in simple unit cell = \( \frac{1}{8} \times 8 = 1 \) atom

2) **Face centered cubic (fcc) unit cell**:-In a face centered unit cell there are eight atoms at the corners and six atoms at each face of the cube. Each corner atom is shared by eight unit cells and the atom at the face is equally shared by two unit cells, hence, it contributes \( \frac{1}{2} \) atom to each unit cell.

Number of atom in fcc unit cell = \( \frac{1}{8} \times 2 + 6 \times \frac{1}{2} = 1 + 3 = 4 \) atoms

3) **Body Centered cubic (bcc) unit cell** :-In body centered cubic unit cell there are eight atoms at the corners of the cube and
one atom at the centre. As each corner atom contribute $1/8$ atom and one at the centre belong to the particular cell only.

Number of atom in bcc unit cell = \( \frac{1}{8} \times 8 + 1 = 2 \) atoms

**The density of Unit cell**

The density of unit cell can be calculated by knowing the edge length of unit cell, type of crystal structure and atomic mass of atoms.

Let the edge of cubic cell = \( a \) cm.

volume of unit cell = \( a^3 \)

since density \( (\rho) = \frac{\text{Mass of Unit cell}}{\text{Volume of Unit cell}} \)

Mass of Unit cell = No. of atom in Unit cell x mass of each atom

\[ = n \times \frac{\text{Atomic mass (M)}}{\text{Avogadro’s number (N)}} \]

Density of Unit cell \( (\rho) = \frac{nM}{a^3N} \text{ g/cm}^3 \)

**Bragg’s Law**

Bragg’s (1913) discovered a mathematical relation to determine the interplaner distances from x-ray diffraction patterns. This relation is known as Bragg’s Law. They showed that –

i) The x-ray diffraction from atoms is crystalline planes follows law of reflection.

ii) The two rays reflected by a successive planes will be in phase i.e. the extra distance travelled by a second ray is integral multiple of wavelength.

**Derivation of Bragg’s Law**

The horizontal lines represent parallel planes in the crystal structure separated by a distance ‘\( d \)’. When x-rays are incident on crystal plane, some of them will be reflected from upper most plane while other will absorbed and get reflected from successive planes. The wave reflected from different layers will be in phase with one another. Only if path
difference in path length of successive planes in equal to the integral multiple of wavelength ($\lambda$)

$\angle CAB = \angle BAD = \theta$

$\triangle ABD$ –

$\sin \theta = \frac{BD}{AB} = \frac{BD}{d}$

$BD = d\sin \theta$

$\triangle ABC$

$\sin \theta = \frac{BC}{AB} = \frac{BC}{d}$

$BC = d\sin \theta$

Path difference ($\delta$) of XAX’ and YBY’ is

$\delta = BD + BC$

$\delta = d\sin \theta + d\sin \theta$

$\delta = 2d\sin \theta$

From the wave reflected from the first and second layer to be in same phase i.e. path difference $\delta$ must be the integral multiple of $\lambda$

i.e. $n\lambda = 2d\sin \theta$ Where $n = 1, 2, 3, \ldots$

This is known as Bragg’s Law.