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Chemical Bonding

1.1 INTRODUCTION

Atoms combine to form molecules. The combining power of atoms to form molecules is called valency (Latin word *valentia*; meaning strength). Valency of an atom indicates the number of atoms of hydrogen which combine with one atom of an element. This definition of valency has, however, failed in case of carbon, as the valency in the compounds C₂H₂, C₂H₄, C₂H₆ and CH₄ varies from 1 to 4.

With the advancement of knowledge about atomic structure, it was realized that electrons in atoms were primarily involved in chemical combinations. According to the *Lewis octet rule*, atoms of all elements have a tendency to acquire an electronic configuration similar to that of inert gases because it represents the most stable electronic configuration. All atoms having unstable or incomplete outer shell have a tendency to gain or lose electrons so as to acquire an electronic configuration of the nearest inert gas in the Periodic Table. It is this tendency of atoms to complete and hence stabilize their outermost orbit of electrons which is mainly responsible for chemical combination between the atoms.

Thus, according to the *electronic theory of valency* ‘a chemical bond is formed as a result of electronic interactions. It may, however be noted that a molecule is formed only when electrons of the constituent atoms interact in such a way that the potential energy is lowered. Greater the lowering of potential energy, greater is the strength of the bond.

Subsequently, the ‘wave mechanical theory’ was developed which gave logical understanding of bonding between atoms. On the basis of wave mechanical theory, it is also possible to make fruitful predictions regarding the geometrical structure of molecules.

1.2 TYPES OF BONDS

According to the electronic theory of valency the interaction of extranuclear electrons leads to the formation of following types of bonds:

(i) Electrovalent or ionic bond
(ii) Covalent bond
(iii) Coordinate bond

There are mainly three ways by which the atoms may obtain a stable electronic configuration, namely, by gaining, losing or sharing of electrons. We divide all the known elements on electronegativity scale into:

(a) electropositive elements, whose atoms give up one or more electrons readily
(b) electronegative elements, whose atoms take up electrons
(c) elements whose atoms neither lose nor gain electrons
Thus, the following three types of bonds are possible by the different types of combinations of the three types of elements:

(i) Electropositive elements + Electronegative elements → Ionic bond
(ii) Electronegative elements + Electronegative elements → Covalent bond
(iii) Electropositive elements + Electropositive elements → coordinate bond

1.2.1 Electrovalent or Ionic Bond

The ionic bond is formed due to the “electrostatic attraction between stable ions formed by the complete transfer of electrons from one atom to another”, and the combining atoms acquire inert gas configuration. The atom which loses electrons acquires a positive charge, whereas the one which gains electrons becomes negatively charged. These charged atoms are called ions and held together by electrostatic attraction forces. Such a mode of combination of atoms is called electrovalency and the bond formed between the atom is called electrovalent or Ionic bond. The compound thus formed is called an electrovalent or ionic compound.

Atoms having a tendency to lose electrons are called electropositive whereas the atoms which gain electrons are called electronegative. The number of electrons gained or lost by an atom in order to acquire an inert gas configuration gives numerical value of the electrovalency of the atom.

Let us consider the formation of sodium chloride (NaCl) as an example. The electronic arrangement of Na and Cl atoms are:

Na (11) 2, 8, 1 (1s², 2s², 2p⁶, 3s¹)
Cl (17) 2, 8, 7, (1s², 2s², 2p⁶, 3s², 3p⁵)

The electron from the outermost orbit of Na is completely transferred to the outermost orbit of Cl atom. As a result of this transfer, both atoms acquire inert gas structure. The Na becomes Na⁺ (2, 8) and Cl become Cl⁻ (2, 8, 8).

They attain inert gas structure of neon and argon respectively. The two +ve and –ve ions are held together by electrostatic force of attraction acting between them. The formation of NaCl is depicted below:

\[
\text{Na}⁺ (2, 8, 1) + \text{Cl}⁻ (2, 8, 7) \rightarrow \text{Na}⁺ [\text{Cl}⁻]⁻
\]

In the formation of BaCl₂, two electrons from outermost shell of Ba are completely transferred to the outermost orbit of two chlorine atoms. By losing two electrons Ba becomes bivalent Ba²⁺ ion having two positive charges. It combines with two chlorine ions formed from chlorine atoms by accepting one electron each.

\[
:\text{Cl}⁻ \times \text{Ba} \times :\text{Cl}⁻ \rightarrow [\text{Ba}²⁺ \left[\begin{array}{c}
\vdots \\
\vdots \\
\vdots 
\end{array}\right]²⁻]⁻
\]

Other examples of ionic compounds are Cas, KCl, MgCl₂, K₂O etc.
Electrovalent compounds exhibit following properties:

(i) Electrovalent compounds are generally hard solids.
(ii) They have high melting and boiling point.
(iii) Electrovalent compounds are generally sparingly soluble in organic solvents.
(iv) Electrovalent compounds in solid state are poor conductors of electricity. But when dissolved in solvents of relatively high dielectric constant, they exhibit a strong electrical conductivity. They also conduct electricity in the molten state.

1.2.2 Covalent Bond

Formation of molecules by the sharing of electrons between combining atoms is called covalency and the bond formed is called covalent bond or covalent linkage. Compounds containing this type of linkage are called covalent compounds. In covalent bond formation the inert gas configuration of the two concerned atoms is achieved by sharing equal number of electrons.

The sharing of electrons to form chemical bond between two atoms is described by showing pairs of electrons between the bonded atoms. If one pair of electrons is shared, the bond formed is called single bond, whereas sharing of two or three pairs of electrons leads to the formation of double or triple bonds respectively. Due to sharing of electrons, both the bonding atoms acquire inert gas configuration.

Let us consider the formation of hydrogen molecule from two hydrogen atoms. Each hydrogen atom has only one electron and thus its configuration is unstable but when both the hydrogen atoms share their electrons to form a pair of electrons equally shared between the two atoms i.e., the pair of electrons becomes a common property of the two hydrogen atoms; the resulting molecule acquires He configuration.

The covalent bond is represented by a dash (−).

\[
\text{H}_2 + \text{H} \rightarrow \text{H} \cdot \text{H} \quad \text{or} \quad \text{H} \rightarrow \text{H} \\
\left[1s^1\right] \quad \left[1s^1\right]
\]

Similarly, the formation of CCl₄ and CH₄ takes place as below:

\[
\begin{align*}
\text{H} & \cdot \text{H} \cdot \text{H} \cdot \text{H} \\
\text{Cl} & \cdot \text{Cl} \cdot \text{Cl} \cdot \text{Cl}
\end{align*}
\]

\[
\begin{align*}
\text{H} & \cdot \text{H} \cdot \text{H} \cdot \text{H} \\
\text{Cl} & \cdot \text{Cl} \cdot \text{Cl} \cdot \text{Cl}
\end{align*}
\]

Some other examples of the formation of covalent compounds is shown below:

(i) Single bonds:

\[
\begin{align*}
\text{H}_2 & + \text{H} \rightarrow \text{H} \cdot \text{H} \\
\text{Cl}_2 & \rightarrow \text{Cl} \cdot \text{Cl}
\end{align*}
\]
(ii) Double bonds:

\[
\begin{array}{c}
O_2 :\ddot{\text{O}} + :\dddot{\text{O}} \rightarrow O=O \\
\text{CO}_2 \xrightarrow{\text{O}} \text{C} - \text{O} \rightarrow O=C=O
\end{array}
\]

(iii) Triple bonds:

\[
\begin{array}{c}
\text{N}_2 :\dddot{\text{N}} + :\dddot{\text{N}} \rightarrow N≡N \\
\text{C}_2\text{H}_2 \xrightarrow{\text{H}} \text{C} - \text{C} - \text{H} \rightarrow H-C≡C-H
\end{array}
\]

(acetylene)

In covalent compounds the numerical value of covalency of any element in the molecule is the number of electron pairs shared between the atoms. Thus the valency of hydrogen in H\textsubscript{2} is one, oxygen in O\textsubscript{2} is two, nitrogen in N\textsubscript{2} is three and carbon in CH\textsubscript{4} is four.

The covalent bonds are of two types:

(i) Polar covalent bonds

(ii) Non-polar covalent bonds

(A) Polar Covalent Bonds

When a bond is formed between unlike atoms, the bonding electrons will not be equally shared. The resulting bond is a polar covalent bond. e.g., formation of HCl.

\[
\begin{array}{c}
\text{H} \xrightarrow{\text{δ}} \text{Cl} \rightarrow \delta^+ \delta^- \\
\text{H}-\text{Cl}
\end{array}
\]

The shared electrons will be shifted more towards the atom having higher electronegativity and this will result in the accumulation of a −ve charge on it. The other atom will carry an equivalent +ve charge. In the above example of HCl, the chlorine atom acquires small amount of −ve charge because of its higher electronegativity and hydrogen has an equivalent +ve charge. The \(\delta^+\) and \(\delta^-\) represents respectively the small +ve and −ve charge.

(B) Non-polar Covalent Bonds

When a bond is formed between atoms of the same element, the bonding electrons are equally shared on account of equal electronegativity of the atoms. The resulting bond is a non-polar covalent bond. In case of such a bond, the centre of +ve charge coincides with the centre of −ve charge in the molecule.

For example, bonds involved in the formation of H\textsubscript{2}, Cl\textsubscript{2}, O\textsubscript{2}, N\textsubscript{2} etc are non-polar bonds.

\[
\begin{array}{c}
\text{H} \xrightarrow{\text{H}} \text{H} \rightarrow \text{H}-\text{H} \\
\text{Cl} \xrightarrow{\text{Cl}} \text{Cl} \rightarrow \text{Cl}-\text{Cl}
\end{array}
\]

Covalent compounds possess following general characteristics:

(i) Colvalent compounds possess definite geometrical shapes. They exhibit isomerism because covalent bonds are rigid and possess directional characteristics.
(ii) Covalent compounds are mostly liquid and gases. The solid compounds are generally volatile.

(iii) They are highly soluble in organic solvents but slightly soluble in water. Some compounds like HCl and NH₃ readily dissolve in water because they react with water.

\[ \text{HCl} + \text{H}_2\text{O} \rightarrow [\text{H}_3\text{O}]^+ + \text{Cl}^- \]

\[ \text{NH}_3 + \text{H}_2\text{O} \rightarrow [\text{NH}_4]^+ + \text{OH}^- \]

(iv) The melting and boiling points of covalent compounds are relatively low because the forces involved in covalent compounds are less strong than those involved in electrovalent or ionic compounds.

(v) These compounds do not contain ions. Therefore, when dissolved, they do not conduct electricity. They even do not conduct electricity in the molten state.

**Comparison of Electrovalent and Covalent Compounds**

The essential difference between electrovalent and covalent linkages is that in the former case complete transference of electrons between the atoms takes place whereas in the latter case there is no transfer of electrons between the bonding atoms but instead, there is sharing of electrons. Since no transfer of electrons is involved, covalent compounds are non-ionic in nature.

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Electrovalent or Ionic Compounds</th>
<th>Covalent Compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>This type of bond is frequently encountered in inorganic compounds.</td>
<td>This type of bond is frequently found in organic compounds.</td>
</tr>
<tr>
<td>2.</td>
<td>Electrovalent compounds are soluble in water but insoluble in organic solvents</td>
<td>Covalent compounds are soluble in organic solvents and insoluble in water.</td>
</tr>
<tr>
<td>3.</td>
<td>They possess high M.P. &amp; B.P.</td>
<td>They have low M.P. and B.P.</td>
</tr>
<tr>
<td>4.</td>
<td>Electrovalent compounds are not inflammable.</td>
<td>They are inflammable.</td>
</tr>
<tr>
<td>5.</td>
<td>They do not possess any characteristic smell.</td>
<td>They usually possess a characteristic smell.</td>
</tr>
<tr>
<td>6.</td>
<td>In electrovalent compounds reactions are rapid.</td>
<td>In covalent compounds reactions are slow.</td>
</tr>
</tbody>
</table>

1.2.3 **Coordinate Bond**

When, an atom having a complete octet donates a pair of free valence electrons to another atom which is short of two electrons, the resulting bond is known as coordinate bond. Thus both the atoms acquire inert gas configurations.

The atom which donates a pair of electrons is called ‘**donor**’ and the other atom which accepts the electrons is called ‘**acceptor**’. The coordinate bond is similar to covalent bond except that both the shared electrons are donated by one atom. The formation of covalent and coordinate bond is illustrated below:

\[ \text{A}^- + \text{B} \rightarrow \text{A} : \text{B} \quad \text{or} \quad \text{A} - \text{B} \quad \text{(Normal covalency)} \]

\[ \text{A} \bigtriangleup + \text{B} \rightarrow \text{A} : \text{B} \quad \text{or} \quad \text{A} - \text{B} \quad \text{(Coordinate valency)} \]
When one atom furnishes both electrons for the formation of a covalent bond as described above, the process is called ‘co-ordination’.

Since one atom donates an electron pair and the other accepts, the molecule acquires polarity. These bonds, therefore, are also known as ‘semi polar bonds’ or ‘dative bond’. The extent of polarity is larger than that of covalent bonds although less than electrovalent bonds. Coordinate bond is represented by the symbol (→).

Formation of some coordinate compounds is illustrated below:

(i) ammonium ion [NH₄⁺]

(ii) Phosphate ion [PO₄³⁻]

(iii) SO₄⁻ (Sulphate ion)

(iv) Compounds of NH₃ + BCl₃
Following are the main characteristics of coordination compounds:

(i) Coordinate compounds, like covalent compounds, exhibit space isomerism. This is due to directional characteristics possessed by coordinate linkage.

(iii) The B.P. and M.P. of these compounds have intermediate value between electrovalent and covalent compounds.

(iii) They are only slightly soluble in water and most of them are soluble in organic solvents.

(A) Exceptions to the Octet Rule

There are certain stable compounds where the octet rule is not obeyed, that is, their valence shells contain more or less than 8 electrons. The compounds containing less than 8 electrons in the valence shells are called electron deficient compounds such as B$_2$F$_6$, Al$_2$Cl$_6$ etc. On the other hand, the compounds containing more than 8 electrons in the valence shells may be called electron surplus compounds e.g., PCl$_5$, SF$_6$, OsF$_8$ etc.

In an electron deficient compound such as B$_2$F$_6$, the available electrons are insufficient for sharing between the two boron atoms and the six fluorine atoms. Each boron atom has three electrons so that the two boron atoms have six electrons which are just sufficient for binding the three fluorine atoms. It has been suggested that boron atoms in B$_2$F$_6$ complete their octet by accepting a pair of electrons from fluorine atoms. The existence of Al$_2$Cl$_6$ can also be explained on the same basis. The structure of B$_2$F$_6$ and Al$_2$Cl$_6$ are given below:

\[
\begin{align*}
\text{F} & \quad \text{F} \\
\text{B} & \quad \text{B} \\
\end{align*}
\]

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

In has been found that Al$_2$Cl$_6$ and B$_2$F$_6$ exist as dimers.

Since a bond involves one pair of electrons, the phosphorous atom in PCl$_5$ would be surrounded by 10 electrons, the sulphur in SF$_6$ by 12 electrons and the Osmium in OsF$_8$ by 16 electrons. The octet rule can be preserved in these compounds if it is assumed that some atoms are joined by single electron bond or singlet linkage to the central atom. A singlet linkage is formed when an atom in a molecule having complete octet, donates one electron to another atom which it needs to complete its own octet.

The singlet linkage may be assumed as a coordinate linkage formed by donation of one electron as shown below:

\[
\begin{align*}
\text{A} & \quad + \quad \text{B} \\
\end{align*}
\]

\[
\begin{align*}
\text{A} & \quad \text{B} \\
\end{align*}
\]
Structure of some compounds involving singlet linkages are shown below:

(B) Odd Electron Bonds

It has been observed that almost all the compounds of non-transition elements contained an even number of bonding electrons. Very few exceptions like NO, NO₂ etc possess odd number of bonding electrons. Such type of compounds are called Odd Molecules. The odd molecules are classified into following two categories.

(i) One Electron Bond Molecule

In such molecules, only one electron forms the bond, e.g., H₂⁺, Li₂⁺, Na₂⁺, K₂⁺

\[ "\text{H-H} \quad \leftrightarrow \quad [\text{H-H}^+] \]

In general, odd bonds are represented as resonance hybride of two or more structures.

(ii) Three Electron Bond Molecules

Three electron bond is formed when an odd electron of an atom becomes associated with a loan pair of electrons on another atoms

\[ \text{[A .: B]} \]

resonance hybrid structure \( \text{[A . B]} \)

The three electron bond may also be represented by three dots i.e., \( \text{[A . . . B]} \)

e.g. \( \text{He}_2^+ \)

\[ \text{[He . . . He]}^+ \]

resonating structure of \( \text{He}_2^+ \)

\[ \text{[He . . He]}^+ \quad \leftrightarrow \quad \text{[He}^+ . : \text{He]} \]

Such molecules which have three electron bonds in addition to an ordinary electron pair bond is represented as follows:

\[ \text{[A . . . B]} \]

These molecules exhibit strong tendency to dimerise.

(C) Resonance

Carbon dioxide molecule can be represented by the following three electronic structures:

\[ \text{(i) } \text{O=\text{C=O}} \quad \text{(ii) } \text{O=\text{C=O}} \quad \text{(iii) } \text{O=\text{C=O}} \]

There is resonance between these structures. The contribution of structures (i) and (iii) involving triple bond is confirmed by the fact that the carbon to oxygen bond length in \( \text{CO}_2 \) is
slightly smaller than the normal carbon-oxygen double bond. The real structure of carbon dioxide is something intermediate between these structures, which, infact, cannot be represented by the conventional diagrams and is called a 'resonance hybrid'.

Benzene molecules can be represented as follows:

It has been observed that carbon to carbon single bond length is 1.54 Å, the carbon to carbon double bond length is 1.33 Å. In case of benzene, carbon to carbon distance is 1.39 Å which is intermediate between that of a single and a double bond. This shows that actual bonds in benzene are neither single or double but intermediate in character.

The resonance structure should fulfill the following requirements:
(i) Resonance structure should be similar in terms of energy.
(ii) In resonance structures, the constituent atoms should be in the same position.
(iii) These structures should have the same number of electrons pairs.
(iv) These structures should differ only in the location of electrons around the constituent atoms.

1.3 THEORIES OF COVALENT BOND FORMATION

Two theories have been put forward to explain the formation of the bond, viz
(i) Electronic theory of valency and
(ii) Wave Mechanical theory of covalency

1.3.1 Electronic Theory of Valency

G.N. Lewis explained valency in terms of interaction between extranuclear electrons of the combining atoms. It was suggested that during the formation of molecule the combining atoms tend to attain a stable electronic configurations similar to that of inert gases. The inert gases have S2p6 configuration is their outermost shell (except He, 1s2). According to the electronic theory of valency, when atoms combine to form molecules, the electrons in the outermost shells of the atoms tend to acquire inert gas structure (1s2 or S2p6) which has maximum stability and minimum energy. The atoms after bond formation contain eight electrons in their outermost shells.

The interaction of extranuclear electrons leads to the formation of the following types of bonds:
(a) Electrovalent or ionic bond
(b) Covalent bond
(c) Coordinate bond

The above three has already been discussed earlier in details

1.3.2 Wave Mechanical Theory of Covalency

Electronic theory of covalency cannot account for some important characteristics of molecules such as spatial distribution of bonds, i.e., geometry of molecules, the lengths of bonds involved and their strength etc. Wave mechanics provides better understanding of the char-
characteristics of molecules containing covalent bonds. Following two approaches have been evolved:
(i) Molecular orbital (M.O.) theory
(ii) Valence bond (V.B.) theory

1.3.2.1 Molecular Theory of Diatomic Heteromolecules

According to M.O. theory a covalent bond is formed when two half filled orbitals of two atoms come nearer and then overlap each other to form a new bigger orbital known as ‘Molecular Orbital’. The molecular orbital surrounds the atomic nuclei of both the atoms and each of the electrons, which are now paired (one electron from one atomic orbitals) in the molecular orbital, is electrostatically attracted by both the nuclei. It is important to note that energy of the molecular orbital is less than the sum of energies of the two atomic orbitals and consequently the resulting molecule is more stable than the two separate atoms. Like atomic orbitals, the molecular orbitals also obey Paulies exclusion principle and thus one molecular orbital can accommodate only two electrons with antiparallel spins.

We consider below the case of hydrogen molecule on the basis of above theory. We imagines that in the hydrogen molecule there are two nuclei A and B corresponding to two hydrogen atoms. Let \( \psi_A (1s) \) be the wave function of hydrogen atom A and \( \psi_B (1s) \) be the wave function of the electron of atom B. The molecular orbital wave function is expressed as a combination of two atomic wave function as,

\[
\psi_{Mo} = \psi_A (1s) \pm \psi_B (1s)
\]

The expression is applicable to diatomic molecule and this type of approach for obtaining M.O. of a molecule known as Linear Combination of Atomic Orbitals (LCAO).

Furthermore, it must be noted that when two atomic orbitals overlap each other, two molecular orbitals are produced, namely;
(i) **Bonding** orbitals
(ii) **Anti-bonding** orbitals.

These two new molecular orbitals spread over both the atom and either may contain two electrons.

The bonding molecular orbital have lesser energy than the energies of the separate atomic orbitals whereas the antibonding molecular orbital have higher energy than the energies of the two separate atomic orbitals.

Let us consider the 1s orbitals of hydrogen atom degenerated but when they combine to form molecule, they split into two new energy states, one having high energy and the other having lower energy than the original 1s states. This is illustrated in figure 1.1.

![Figure 1.1. Formation of molecular orbitals from atomic orbitals.](C:\DHARM\N-EGC\CH1)
The wave function for these molecular orbitals are given by the following equations:

\[
\psi_s = \psi_{A(1s)} + \psi_{B(1s)} \\
\psi_A = \psi_{A(1s)} - \psi_{B(1s)}
\]

where \(\psi_s\) corresponds to the lower energy state and \(\psi_A\) to the higher energy state.

In the bonding orbital, the electron density is concentrated between the two nuclei whereas in the antibonding molecular orbital, the electron density moves away from the region between two nuclei.

If overlap of the two atomic orbitals has taken place along their major axes, the resulting molecular orbitals is known as \(\sigma\) (sigma) orbital and the bond formed as \(\sigma\) bond.

\[\text{(A) } \sigma \text{ (sigma) and } \sigma^* \text{ (sigma star) Molecular orbitals}\]

In order to understand the meaning of \(\sigma\) and \(\sigma^*\) orbitals, let us consider the M.O. formed by the combination of orbitals of the two hydrogen atoms as shown in figure 1.2.

\[\text{Figure 1.2. Molecular orbital formation by combination of 1s atomic orbitals.}\]

The dots (•) refer to the position of nuclei. The electron density is concentrated between the two nuclei in bonding \(\sigma\) orbital.

In the 'antibonding orbital' the electron density move away from the region between two nuclei. Antibonding orbitals are marked with asterisks (*). In the case of \(\text{H}_2\) molecule, the antibonding orbital is represented as \(\sigma^* 1s\). The subscripts 1s in \(\sigma 1s\) and \(\sigma^* 1s\) denote the atomic orbits from which the molecular orbitals are formed. Furthermore the \(\sigma 1s\) and \(\sigma^* 1s\) orbitals are symmetric about the bond axis or internuclear axis. It is evident that \(\sigma\) bonding M.O. has no nodal plane containing the molecular axis.

On the other hand, if overlapping of two atomic orbitals has taken place sideways i.e., in their parallel axes, the resulting molecular orbitals are known as \(\pi\) (Pi orbitals) and the newly formed bonds as \(\pi\) bonds.

\[\text{(B) } \pi \text{ (Pi) and } \pi^* \text{ (Pi Star) Molecular Orbitals}\]

The formation of molecular orbitals by combination of p-orbitals is shown in figure 1.3.

In case I, \(P_z\) orbitals of atom 1 combine with \(P_z\) orbital of atom 2 to give two M.O.s, \(\sigma P_z\) and \(\sigma^* P_z\) (antibonding). From the figure it becomes clear that both are symmetric around the line joining the two nuclei (bond axis). In case II, the two p-orbitals overlap sidewise and produce two M.O.s, \(\pi p_x\) and \(\pi^* p_x\). The bonding Pi orbital \((\pi p_z)\) possesses a nodal plane containing the molecular axis. The antibonding orbital \((\pi^* P_z)\) has four top like lobes extending outwards from the two nuclei. In the case III, the formation of \(\pi^* p_y\) and \(\pi^* p_y\) takes place in the same manner as that of \(\pi^* p_z\) and \(\pi^* p_z\) respectively. The only difference is that the M.O.s in the former case lie in a plane at right angles to the plane containing the \(\pi^* p_x\) and \(\pi^* p_x\) orbitals.
The bonds formed from end-on-end overlap of orbitals are called \( \sigma \) bonds. Now since two orbitals overlap along their axes, maximum overlapping is possible and hence the bond formed (\( \sigma \)) is strong. A \( \sigma \) bond may be formed by the overlapping of S—S, S—p, p—p, \( \text{sp}^3—\text{sp}^3 \), \( \text{sp}^2—\text{sp}^2 \), \( \text{sp}—\text{sp} \), \( \text{sp}^3—\text{S} \) or \( \text{p} \), \( \text{sp}^3—\text{S} \) or \( \text{p} \) and \( \text{sp}—\text{S} \) or \( \text{p} \) orbitals of two or more atoms.

\[ \sigma \]

On the other hand, the bonds formed from sideways (lateral) overlapping of orbitals are known as \( \pi \) bonds. Now here since the lateral overlapping is only partial, the bonds thus formed are weak bonds. A \( \pi \) bond is formed by the overlap of two orbitals.

\[ \pi \]

The molecular orbitals are schematically represented in an energy level diagram shown in figure 1.6.
(D) Molecular Orbital Energy Levels

Just as there is an order of filling atomic orbitals, there is also an order for filling of molecular orbitals. In deriving molecular configuration, Aufbau’s principle, Hund’s rule and Pauli’s exclusion principle are applicable as in the case of atoms. The order of filling of molecular orbitals has not been derived on theoretical grounds but is based on spectroscopic evidence. Accordingly, following order of filling exists in the case of simple homonuclear diatomic molecules: $\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \sigma 2px < \pi 2py = \pi^* 2py < \pi^* 2pz < \sigma^* 2px$. The energy level diagram for the molecular orbitals is given in figure 1.6.

![Energy level diagram for molecular orbitals](image)

Figure 1.6. The energy level diagrams for the M.O.’s of the homonuclear diatomic molecule.
According to Molecular Orbital theory:

(i) During bond formation, the half filled orbitals with opposite spins of the two combining atoms merge to form two M.O.—one bonding M.O and one anti M.O. The energies of combining atomic orbitals, however should be of similar magnitude.

(ii) A bonding M.O. has lower energy and greater stability than the atomic orbitals from which it is formed while antibonding M.O. has higher energy and lower stability than the atomic orbitals from which it is formed.

(iii) M.O. formation is always accompanied by loss of energy.

(iv) Two s or p orbitals can overlap end to end to form one sigma bonding M.O. (σ) and one sigma antibond M.O. (σ*).

(v) Two p orbitals can overlap sideways to form one pi (π*) bonding M.O and one pi (π*) antibonding M.O.

(vi) When M.O. have the same energy, the electron enters each orbital with parallel spins, before pairing occurs (Hund’s Rule).

(vii) The energy of σ-type bonding orbitals are lower than those of π-type orbitals.

(viii) σ 2p bonding orbital lies at a lower energy than π 2p bonding orbital. This sequence is correct, when the energy difference between 2s and 2p is large as in O, F and Ne. Hence the energies of M.O.s formed in O₂, F₂ and Ne₂ increases as follows.

\[
\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \sigma 2p_x < \pi 2p_x = \pi^* 2p_y < \sigma^* 2p_z
\]

(ix) When the energy difference between 2s and 2p is smaller as in Li through N, the reversal energies of σ2p and π2p takes place. The energies of M.O.’s of homonuclear diatomic species of elements from Li through N₂ actually increases as follows:

\[
\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \sigma 2p_x = \sigma^* 2p_y < \pi 2p_y < \sigma^* 2p_z
\]

(E) Molecular Orbital Configuration & Energy Diagrams of some Molecules

(i) \(H_2\) Molecules

M.O. configuration: \(\sigma (1s^2) \sigma^* (1s^*)\)

Hence B.O. = \[ \frac{2 - 0}{2} \]
= 1

M.O. Diagrams:

(ii) \(Li_2\)

Electronic configuration of Li = 1s\(^2\), 2s\(^1\)
M.O. configuration of \(Li_2\) = \(\sigma (1s^2) \sigma^* (1s^*) \sigma (2s^2)\)

Hence B.O. = \[ \frac{4 - 2}{2} \]
= 1

M.O. Diagrams
Since all electrons are paired, thus the molecule is diamagnetic.

(iii) $O_2$

Electronic configuration: $1s^2, 2s^2, 2p^4$

M.O. configuration: $\sigma 1s^2, \sigma^* 1s^2, \sigma^* 2s^2, \sigma 2p^2, \pi 2p^2, \pi^* 2p^2, \pi^* 2p^2$
B.O. = \frac{10 - 6}{2} = 2

Since two electrons are unpaired, thus the molecule is paramagnetic

(F) Bond Order

It is defined as one half of the difference between the number of electrons in bonding M.O.’s and the number of electrons in antibonding M.O.’s. The bond order is given as

\text{Bond order} = \frac{\text{No. of bonding electrons} - \text{No. of anti bonding electrons}}{2}

Bond order is a measure of the stability of a molecule. Higher the bond order greater the stability of the molecule. Zero bond order means that formation of the molecule will not take place.

(G) Bond Length

Bond length is also known as interatomic distances. It may be defined as “the distance between the centre of nuclei of the two bonded atoms”. The bond length depends largely on the type of bond present. The bond lengths in ionic (electrovalent) compounds can be determined from the radii of the two concerned ions (ionic radii). Bond length is usually expressed in Angstrom units. \(1\text{Å} = 10^{-8}\text{ cm}\).

(H) Bond Angles

A bond angle is defined as “the angle between the direction of two covalent bonds”. It may be represented by the sign \(\theta\). Most of the polyatomic molecules (except of few such as \(\text{CO}_2\) and \(\text{CS}_2\) which are linear), are angular with a bond angle generally somewhat greater than 90°.

(I) Bond Energy

The amount of energy associated with each bond as it exists in a molecule is called the bond energy. It represent the contribution of the bond to the total binding energy present in the molecule and thus the summation of bond energies of all the bonds in a molecule gives the heat of formation of the molecules from its atoms.

1.4 BOND THEORY OF BONDING IN METAL

Metallic bond results from a delocalized covalent bonding by the overlap of valence-orbitals between nearest neighbour atoms. Thus, metallic crystal lattice consists of positive ions called kernels, permeated by a cloud of valency electrons called electron gases, as illustrated in figure 1.7.

![Figure 1.7. Diagrammatic representation of metallic bonding.](image-url)
The binding force is attraction between kernels of atoms (atom minus valency electrons) and the electron cloud. In other words, all valency electrons belong to the crystal as a whole. These electrons are free to migrate throughout the crystal lattice, thereby giving rise to high electrical conductivity to metals. The high reflectance of metal arises, due to the ease with which the free electrons get accelerated by high frequency radiations and then, radiate immediately, virtually all the energy of the incident radiation absorbed.

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

There are three major theories applied for bonding in metals, viz;
(i) Free electron theory, (ii) V.B. Theory, and (iii) M.O. Theory.

1.4.1 Free Electron Theory

According to this theory each atom in a metal crystal loses all its valency electrons due to low ionization energy of the metal atoms. These electrons form an electron pool or gas. Now a metal is regarded as a group of +ve metal ions are believed to be held together in a regular geometric pattern by this electron pool or gas. The force that binds a metal ion to the mobile, electrons within its sphere of influence is known as metallic bond.

1.4.2 Valence Bond Theory

According to this theory, the metal bonding is essentially covalent in origin and metallic structure involves resonance of electron pair bonds between each atom and its neighbours. A potassium atom with 2S1, i.e., one electron in its outer shell, may be shared with one of its neighbours forming a normal two-electron bond.

\[
\begin{align*}
\text{K} & \quad \text{K-K} & \quad \text{K-K} & \quad \text{K-K} & \quad \text{K-K}^+ \\
\text{K} & \quad \text{K-K} & \quad \text{K-K} & \quad \text{K-K} & \quad \text{K-K} \\
& \quad \text{K} & \quad \text{K} & \quad \text{K} & \quad \text{K} & \quad \text{K}^+ \\
\end{align*}
\]

These are some of the resonance structures of K which account for large resonance energy and hence large cohesive force.

1.4.3 Molecular Orbital Theory

According to this theory, metallic bond results from the delocalisation of the free electrons orbital over all the atoms of a metal structure.
Let us consider the construction of a crystal of a sodium metal by adding Na atoms one at a time, forming first Na$_2$, then Na$_3$, Na$_4$ and Na$_N$ (where N is a very large number of the order of $10^{23}$ in 1 cm$^3$ of a solid).

In diatomic Na$_2$ molecule, each Na atom has electronic configuration [Ne] 3s$^1$ with a single 3s valence electrons. Two 3s- atomic orbitals, one from each Na atom overlap to form two molecular orbitals $\sigma$ (3s) & $\sigma^*$ (3s).

![Diagram showing overlap of atomic orbitals](image)

There are just two valence electrons, which will occupy lower energy bonding molecular orbitals ($\sigma$ 3s). The antibonding M.O. $\sigma^*$ 3s is vacant.

With the help of Molecular orbital theory of metals, materials can be classified into following three categories, depending on the energy gap between the valence and conduction bonds:

(a) Conductors,  
(b) Insulators, and  
(c) Semiconductors.

The above three energy bonds are diagrammatically represented in figure 1.8.

![Energy band diagram](image)

**Figure 1.8.** Energy band in (A) conductors, (B) insulators and (C) semiconductors.

In conductors (metallic elements) either the valence bands and conduction bands overlap or the valence band is only partly full. As the filled and unfilled molecular orbitals are not separated by significant gap, hence perturbation can occur readily.

In insulators (non-metallic elements), there is a large band gap between the filled valence bands and empty conduction band. Therefore electrons cannot be promoted from the V.B. to C.B. where they could move freely.
Semiconductors are of two types, intrinsic and extrinsic semiconductors. Intrinsic semiconductors have small energy gap between the filled V.B. and empty C.B. sufficient to promote an electron from VB to CB. The hole left in the V.B. and the promoted electrons in the CB both contribute towards conductivity. It is obvious that number of electrons promoted to CB increases with rise in temperature, thus conductivity of semiconductors increases with temperature. The conductance of semiconductors can be improved by doping. Doping means treatment of Si and Ge with impurity atoms of group III and V giving respectively p-type and n-type semiconductors. Basically the band from the impurity lies in between the VB and CB, so that electrons may be easily excited from VB to impurity band and hence conductance increases.

1.5. HYDROGEN BONDING

The attraction between a hydrogen atom attached to an electronegative atom in one molecule and an electronegative atom in another is called the hydrogen bond and the phenomenon is known as hydrogen bonding. The O—H and N—H bonds are polar in which the hydrogen has a partial positive charge. This can interact with the non bonding electrons of some other electronegative atom i.e. oxygen or nitrogen. Due to the electrostatic attraction, a very weak hydrogen bond is formed. The hydrogen bond is denoted by dotted line (......), e.g.,

![Figure 1.9. Hydrogen bonding in water molecule.](image)

Hydrogen bond is very weak and possesses a bond energy in the range of 2–10 K cal/mol. Hydrogen bonding occurs in compounds like alcohols, water, aldehydes, ketones, ethers, ammonia, amines, carboxylic acids, hydrogen fluoride etc.

The increasing order of hydrogen bonding in some atoms is:

\[ S < Cl < N < O < F. \]

1.5.1. Types of Hydrogen Bonding

There are two types of hydrogen bonds viz., intermolecular and intramolecular.

**Intermolecular Hydrogen Bond**

Intermolecular hydrogen bonding occurs in between two or more molecules of the same or different types. Boiling point increases due to the hydrogen bonding, e.g., The B.P. of \( \text{H}_2\text{S} \) is
40°C while that of water is much higher i.e. 100°C. This increase in B.P. of water is explained on the basis that association of water molecules takes place in the liquid state. The hydrogen bonds link the water molecules together to form a huge molecular aggregate. Extra energy is thus required to break the hydrogen bonds which raise its boiling point. Hydrogen sulphide (H₂S), on the other hand, lacks this association. HF is a liquid at room temperature than other hydrides of halogens because of hydrogen bond formation in HF. Propylamine (BP 49°C) boils higher than trimethylamine (BP 3.5°C) for the same reasons. Ethanol (BP 78.3°C) boils higher than the isomeric compound dimethyl ether (− 24°C) and phenol (BP 182°C) boils higher than toluene (110°C) because of hydrogen bonding.

Intermolecular hydrogen bond formation lowers the strength of an acid, e.g., HBr is weaker than HI and H₂O is weaker than H₂S. For a substance to be soluble in water, it should be able to make hydrogen bond with water, e.g. ethanol and methanol are miscible with water in all proportions because of coordination with water, while ethers, higher alcohols and hydrocarbons are not soluble in water because they can not associate with water.

**Intramolecular Hydrogen Bonding**

This type of bonding occurs within the same molecule. A large number of molecules are capable of forming intramolecular hydrogen bond between two groups present in the same molecule. This results in the formation of a five or six membered rings. This type of association also alters the properties of molecule, e.g., phenol on nitration gives two products i.e., o- and p-nitrophenols. The isomers can be separated by steam distillation as the o-isomer a liquid distils over while the p-isomer remaining in the flask is a solid. This difference in BP of the two isomers has been explained on the occurrence of intramolecular hydrogen bonding in the isomer, resulting in a six membered ring and intermolecular hydrogen bonding in p-isomer, with no ring formation.

Some examples of intramolecular hydrogen bonding are as given below:

\[
\text{O} \quad \text{N} \quad \text{O} \quad \text{H} \\
\text{O} \quad \text{N} \quad \text{O} \quad \text{H}
\]

Intramolecular hydrogen bonding increases the strength of an acid.

**PROBLEMS**

1. Discuss the salient features of molecular orbital theory of bonding. How does it differ from valence bond theory.
2. Explain valence shell electron pair repulsion theory on the basis of bond angle of methane, ammonia and water.
3. Calculate the bond order in B₂, N₂, O₂, F₂, and NO.
5. What is the effect of temperature and impurities on conductivity of semiconductor?
6. State the factors which favour covalency.
7. What is hybridisation? Calculate % $S$ orbital character of a hybrid orbital if bond angle between hybrid orbital is 105°.
8. State differences between $\sigma$ (Sigma) and $\pi$ (Pi) bonds.
9. Calculate number of $\sigma$ (Sigma) and $\pi$ (Pi) bonds in $C_2H_2$, $C_2H_4$, $CO_3^{--}$, $NH_3$, $PCl_5$.
10. Predict shape, bond angle, dipole moment and hybridisation of the following compounds on the basis of VSEPR theory:
    \[ Ag(CN)_2^+, XeO_3, H_2O, PCl_5, XeF_4 \]
11. Predict shape, bond angle dipole moment and hybridisation of the following compounds on the basis of VSEPR theory:
    \[ SO_4^{--}, NH_4^+, BF_4^-, XeO_4, NH_3 \]
12. Explain paramagnetic nature of $O_2$ and its less stability in comparison to that of $N_2$.
13. NO$_2$ is coloured but N$_2$O$_4$ is colourless. Explain
14. Write order for the filling of electrons in various molecular orbitals.
15. What is meant by ‘Bond order’? Give a formula to calculate it. Calculate bond order for NO.
16. Explain formation of bonding and antibonding molecular orbitals on the basis of wave function.
18. Which of the following is paramagnetic:
    \[ O_2^-, O_2^{--}, N_2, C_6H_6, CO_3^{--} \]
20. Arrange the following in the decreasing order of acidity and C—H bond length: $CH_4$, $C_2H_6$, $C_2H_4$, $C_2H_2$