UNIT 4: CHEMICAL BONDING- I

CONTENTS:

4.1 OBJECTIVES

The objective of writing the text of this unit is to enable the readers to understand various facts regarding the driving force that makes the isolated atoms to combine to form the polyatomic molecules or ions as well as to find the answers of certain interesting questions such as: What is a chemical bond? What happens to the energy of the atoms and the molecules? What happens in terms of electronic structure, while bond formation takes place?

Why do the group 18 elements, i.e. the noble gases, generally not participate in bond formation and suffer from lack of reactivity while almost all other elements do so? etc.

4.2 INTRODUCTION

The atoms are said to combine together because of the following two main reasons:

(i) Concept of lowering of energy

It has been observed that the aggregate (or the molecules) are lower in energy than the individual atoms from which they have been formed. This means when the individual atoms combine to form molecules through a bond, the potential energy of the combining atoms decreases and the resulting molecules are more stable than the free atoms. This energy difference between the free atoms and bonded atoms (or molecules) is generally 40kJ mol^{-1} or more. It follows from this that the process of bond formationbetween the atoms decreases the energy of the molecule formed from these atoms and forms a system of lower energy and greater stability.

(ii) Electronic theory of valence (the octet rule)

The atoms of the noble gases-helium to radon- do not, except a few cases, react with any other atoms to form the compounds and also they do not react with themselves. Hence they stay in atomic form. These atoms are said to have low energy and cannot be further lowered by forming compounds. This low energy of noble gas atoms is associated with their outer shell electronic configuration, i.e. the stable arrangement of eight electrons (called octet). It has also been established that the two electrons in case of helium atom (called doublet) is as stable as an octet present in other noble gas atoms. The chemical stability of the octet of noble gases led chemists to assume that when atoms of other elements combine to form a molecule, the electrons in their outer shells are arranged between themselves in such a way that they achieve a stable octet of electrons (noble gas configuration) and thus a chemical bond is established between the atoms.

This tendency of the atoms to attain the noble gas configuration of eight electrons in their outer shell is known as octet rule or rule of eight and when the atoms attain the helium configuration, it is called doublet rule or rule of two. This octet rule was later called **"Electronic Theory of Valence"**.

It may be noted here that in the formation of a chemical bond, atoms interact with each other by losing, gaining or sharing of electrons so as to acquire a stable outer shell configuration of eight electrons. This means, an atom with less than eight electrons in the outer shell is chemically active and has a tendency to combine with other atoms. Accordingly, three different types of bonds may exist in the molecules/aggregates.

4.3. COVALENT BOND

A covalent bond is formed between the two combining atoms, generally of the electronegative non-metallic elements by the mutual sharing of one or more electron pairs (from their valence shell). Each of the two combining atoms attains stable noble gas electronic configuration, thereby enhancing the stability of the molecule. If one electron pair is shared between the two atoms, each atom contributes one electron towards the electron pair forming the bond. This electron pair is responsible for the stability of both the atoms. A covalent bond is denoted by the solid line (-) between the atoms. Depending on the number of shared electron pairs i.e. one, two, three etc. electron pairs between the combining atoms, the bond is known as a single, double, triple etc. covalent bond. For example,

H:H H-H
Cl:Cl Cl-Cl **single bond**
H:Cl H-Cl
O::O O=O **double bond**
N:::N N≡N **triple bond** **multiple bond**

In the molecules, the bond strength and bond length has been found in the following order:

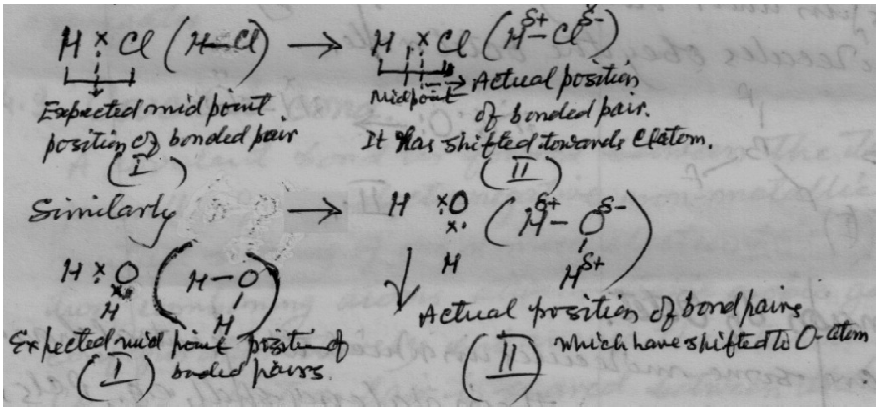
Bond strength: triple bond > double bond > single bond
Bond length: triple bond < double bond < single bond

It may be noted that the covalent bond formation between multielectron atoms involves only the valence shell electrons that too, the unpaired electrons. Thus O-atom has two unpaired electrons in its valence shell and N-atom has three unpaired electrons thereby forming two and three bonds with themselves or other atoms.

Polar and non-polar covalent bond

In the examples given above, most of the bonds *viz.* single, double and triple covalent bonds, have been shown to be formed between the like atoms such as H-H, Cl-Cl, O=O and N≡N in H_2, Cl_2, O_2 and N_2, respectively. The bonded atoms in these molecules attract the bonding or shared pair of electrons by equal forces towards themselves due to equal electronegativity of the atoms. Hence the bonding pair of electron lies at the mid point of the internuclear distance (or bond distance). This type of bond is known as the non-polar covalent bond.

But if the covalent bond is formed between two unlike atoms of different elements, e.g. HCl, H_2O, NH_3 etc., the shared pair of electrons will not be equally attracted by the bonded atoms due to electronegativity difference. It shifts towards more electronegative atom and hence moves away from less electronegative atom. This develops small negative charge on more electronegative atom and equal positive charge on less electronegative atom. Such a molecule is called a polar molecule (this is different from ionic bond) and the bond present in such molecules is known as polar covalent bond. For example,



4.3.1. Valence Bond Theory (VBT) and its limitations:

This theory was put forward by Heitler and London in 1927 to explain the nature of covalent bond. They gave a theoretical treatment of the formation of the bond in H_2 molecule and the energy changes taking place therein. Later, it was extended by Pauling and Slater in 1931 to account for the directional characteristics of the covalent bond.

The main points called the postulates of this theory are given below:

(i) The atoms involved in the bond formation maintain their individuality(identity) even after the bond is formed i.e. in the molecule.

(ii) The bond is formed due to the overlapping of half filled atomic orbitals (or the interaction of electron waves) belonging to the valence shell of the combining atoms as these approach each other. Thus the spins of the two electrons get mutually neutralised. The electrons in the orbitals of inner shells remain undisturbed.

(iii) The filled orbitals (i.e. containing two electrons) of the valence shell do not take part in the bond formation. However, if the paired electrons can be unpaired without using much energy, they are first unpaired by promoting to the orbitals of slightly higher energy and then can take part in bonding. For example, N can form NCl_3 only retaining a lone pair while P can form both PCl_3 and PCl_5.

(iv) The electrons forming the bond undergo exchange between the atoms and thus stabilize the bond.

(v) The strength of the covalent bond depends on the extent to which the two atomic orbital overlap in space.

This theory is based on two main theorems which are:

(a) If $\Psi_A(1)$ and $\Psi_B(2)$ are the wave functions of the orbitals containing electrons in two isolated independent atoms A and B with energies E_A and E_B, respectively then the total wave function Ψ of the system can be given as a product of wave functions of two atoms, i.e.

$$\Psi = \Psi_A(1).\,\Psi_B(2) \qquad \ldots\ldots(4.1)$$

and the energy of the system by

$$E = E_A + E_B \qquad \ldots\ldots.(4.2)$$

Where (1) and (2) indicate two electrons belonging to atoms A and B.

(b) If a system can be represented by a number of wave functions such as Ψ_1, Ψ_2, Ψ_3 ……, then the true wave function Ψ can be obtained by the process of linear combination of all these wave functions as:

$$\Psi = N(C_1\Psi_1 + C_2\Psi_2 + C_3\Psi_3 + \ldots\ldots) \qquad \ldots..(4.3)$$

Where N is normalization constant and C_1, C_2, C_3…are the coefficients indicating the weight of each of Ψs. They are so adjusted as to give a state of lowest energy. The squares of the coefficients may be taken as the measure of the weight of each wave function to total wave function.

The valance bond theory was first applied to the formation of H_2 molecule. If the two H-atoms, *viz*. H_A and H_B are infinitely apart from each other, there is no interaction at all but if these are brought close together, H_A- H_B covalent bond is formed and the energy of the system is decreased. Now if the orbitals of the two H-atoms are represented in terms of wave functions Ψ_A and Ψ_B, then the wave function for the system $H_A.H_B$ can be written as

$$\Psi = \Psi_A(1).\,\Psi_B(2) \qquad \ldots\ldots(4.1 \text{ as given above})$$

Where electrons belonging to H_A and H_B are 1 and 2.

But once the bond is formed, the electrons 1 and 2 have equal freedom to get associated with either of the H-atoms. Thus due to the exchange of electrons between H-atoms, two possible covalent structures of H_2 molecule may shown as $H_A(1).H_B(2)$ and $H_A(2).H_B(1)$. The wave functions of these structures are $\Psi_A(1).\ \Psi_B(2)$ and $\Psi_A(2).\ \Psi_B(1)$ respectively. Now the true wave function for H_2 molecules can be obtained by linear combination of the wave functions for the two covalent structures. This can be done in two ways:

(i) When the combination of these wave functions takes place in a symmetric way, i.e. by addition process, symmetric wave function Ψ_s is obtained:

$\Psi_s = \Psi_A(1).\ \Psi_B(2) + \Psi_A(2).\ \Psi_B(1)$ ……..(4.4)

This is also known as covalent wave function, Ψ cov.

(ii) When the combination of the above wave functions takes place in a asymmetric way i.e. by subtraction process, asymmetric wave function, Ψ_a, is obtained: $\Psi_a = \Psi_A(1).\ \Psi_B(2) - \Psi_A(2).\ \Psi_B(1)$ …….(4.5)

The value of Ψ_s does not change by exchange of electrons 1 and 2 but that of Ψ_a changes in this process. The two situations are presented graphically as follows: ***(Fig 4.1)***

The curve s is for addition process and curve a is for subtraction process of the wave functions. The calculated value of r_o for the minimum energy state i.e. the bonding state is 87 pm against the experimental value of 74 pm.

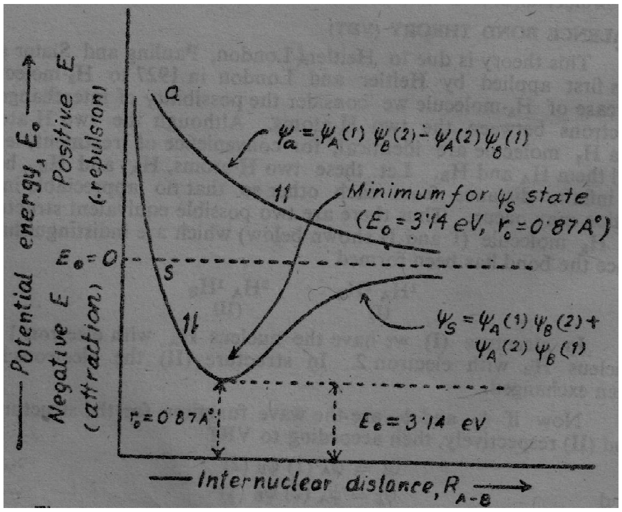


Fig 4.1

Pauling has suggested that the bond between two H-atoms in H_2 molecule is not absolutely covalent, it rather has partial ionic character. He proposed two ionic structures for H_2

molecule in which both the electrons 1and 2 are either attached to H_A or H_B as given below,

$H_A(1,2).\ H^+_B \qquad H^+_A.H_B(1,2)$

If the above wave functions for these structures are $\Psi_{(1)}$ and $\Psi_{(2)}$,

then $\Psi_{(1)}= \Psi_A(1).\ \Psi_A(2)$ …..(4.6)

And $\Psi_{(2)}= \Psi_B(1).\ \Psi_B(2)$ ……(4.7)

The consideration of ionic structures as given above of H_2 molecule converts the equation 4.4 to

$\Psi s=[\Psi_A(1).\ \Psi_B(2) + \Psi_A(2).\ \Psi_B(1)] +\lambda\ [\Psi_{(1)}+\Psi_{(2)}]$

or $\Psi s=[\Psi_A(1).\ \Psi_B(2)+ \Psi_A(2).\ \Psi_A(1)] + \lambda[\Psi_A(1).\ \Psi_A(2)+ \Psi_B(1).\ \Psi_B(2)]$

..(4.8)

or $\Psi s = \Psi cov. + \Psi ionic$ …..(4.9)

the coefficient $\lambda$is used in equation 4.8 is a measure of the degree to which the ionic forms contribute to the bonding. Thus three important contributions to covalent bonding may be summarized as follows:

(i) Delocalization of electrons over two or more nuclei

(ii) Mutual screening

(iii) Partial ionic character.

Limitations of Valence Bond theory:

i) The formation of coordinate covalent bond (also known as dative bond) cannot be explained on the basis of this theory because according to this theory a covalent bond is formed as a result of overlapping of half filled orbitals of the combining atoms and the paired orbitals of the atoms do not take part in normal covalent bond formation.

ii) The odd electron bond formation between the atoms cannot be explained by this theory because a covalent bond is an electron pair bond means two electrons are required for a bond.

iii) This theory is unable to explain the paramagnetic behaviour of oxygen molecule because paramagnetism is a property caused by the presence of unpaired electrons and in an oxygen molecule, according to VBT, two electron pair bonds are present between the oxygen atoms and hence it should be diamagnetic.

iv) In some molecules, the properties like bond length and bond angles could not be explained by assuming simple overlapping of atomic orbitals of the atoms.

4.3.2 Directional characteristics of covalent bond:

The covalent bonds are directed in space. This fact is evidenced by the stereoisomerism and a wide variety of geometrical shapes shown by the covalent compounds. It is also possible to measure the actual bond angles between covalent bonds in the molecules because of the directional nature of bonds. An important fact about the covalent bonds is that these are formed by the overlapping of pure as well as hybridised atomic orbitals. All these atomic orbitals except the pure s-orbitals, are oriented in the particular directions which determine the direction of covalent bonds i.e. the direction in which the overlapping orbitals have the greatest electron density. From this discussion we can conclude that it is the directional nature of p, d and f orbitals which accounts for the directional nature of the covalent bond. For example, the three p-orbitals are directed along the three axes x,y and z and the bonds formed by their overlapping are also directed towards the three axes. Though the s-orbitals are spherically symmetrical around the nucleus, their overlapping along the molecular axis gives a bond in that direction.

Let us discuss the modes of overlapping of pure and some of the hybridised atomic orbitals:

(i) **s-s overlapping**

This type of overlapping occurs between the s-orbitals of the combining atoms thereby giving the s-s covalent bond. This type of overlapping always occurs in the direction of molecular or internuclear axis.

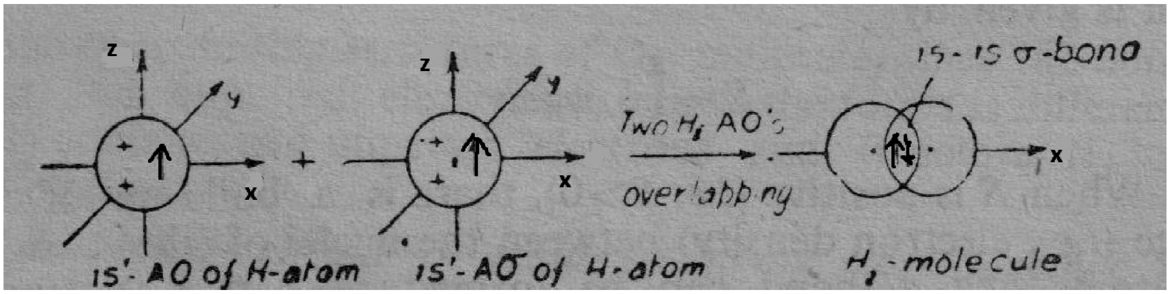


Fig 4.2 ovrelapping of two s-orbitals along molecular axis

(ii) **s-p overlapping**

The overlapping taking place between the s-orbital of one atom and p-orbital of another atom is called s-p overlapping. The resulting bond is the s-p covalent bond formed in the direction of the orientation of p-orbital taking part in overlapping.

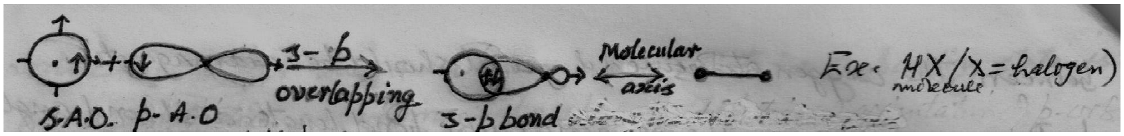


Fig 4.3 *overlapping of s and p orbitals along molecular axis*

(iii) p-p overlapping

When the p-orbital of one atom overlaps with the p-orbital of another atom, this process is called p-p overlapping and the bond so formed is known as p-p covalent bond. The necessary condition for this type of overlapping is that the p-orbitals must be of the same type, i.e. p_x and p_x, p_y and p_y and p_z and p_z. The p_x-p_y or p_x-p_z type of overlapping does not occur.

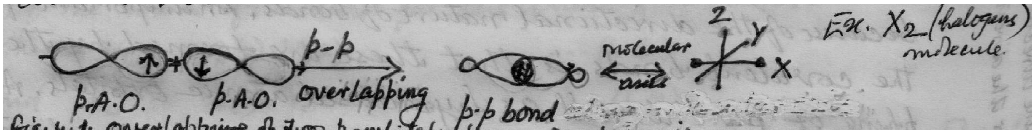


Fig 4.4 *overlapping of two p-orbitals along molecular axis*

If an atom possesses two or three half filled orbitals, they can simultaneously overlap with another similar atom (or other atoms as well) thereby forming multiple bonds (both σ and π), for example oxygen molecule.

Similarly bonding in N_2 can be explained

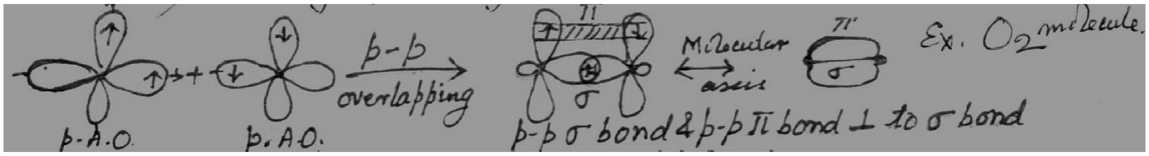


Fig 4.5 *overlapping of orbitals forming σ and πbonds*

(iv) Overlapping of the hybrid orbitals with pure atomic orbitals

The s and p-orbitals may overlap with hybrid orbitals to give the directional covalent bonds such as s-sp(B_eH_2), s-sp^2(BH_3 ,C_2H_4), s-sp^3 (CH_4 and higher alkanes), p-sp (B_eCl_2), p-sp^2 (BCl_3), p-sp^3 (CCl_4), p-sp^3d (PCl_5), p-sp^3d^2 (SF_6) p-sp^3d^3(IF_7) etc. bonds in the directions of hybrid orbitals. d and f - orbitals in non-metallic elements (which mostly form covalent compounds) do not generally take part in overlapping as such to form covalent bonds but d-orbitals may participate in hybridisation, e.g. in PCl_5, SF_6, higher intehalogens etc. and form covalent bonds by the overlapping of hybrid orbitals with atomic orbitals in the directions of hybrid orbitals.

(v) Overlapping of the hybrid orbitals among themselves. This type of overlapping mainly occurs among the organic compounds, e.g. sp-sp(C_2H_2), sp^2-sp^2(C_2H_4), sp^3-sp^3(C_2H_6) etc. Here only the overlapping of hybrid orbitals with themselves has been given.

4.3.3 Sigma (σ) and pi (π) covalent bonds:

σ Covalent bonds

The covalent bond formed between the two atoms by axial or head on overlapping of pure or hybrid atomic orbitals belonging to valence shells of the atoms is called a σ bond. Pure s-orbitals of the atoms on overlapping with s or p atomic orbitals or hybrid orbitals of other atoms always form σ bonds. Pure p-orbitals of the atom when overlap with s and p-orbitals (of the same symmetry) or hybrid orbitals of other atoms also form σ bonds. d and f- orbitals by themselves seldom take part in σ bond formation through the d-orbitals are sometimes involved in hybridisation and thus form a σ bonds, e.g. PCl_5, SF_6, IF_7 etc. The overlapping of hybrid orbitals between two atoms always gives σ bond.

(i) Pure atomic orbital – pure atomic orbital overlapping

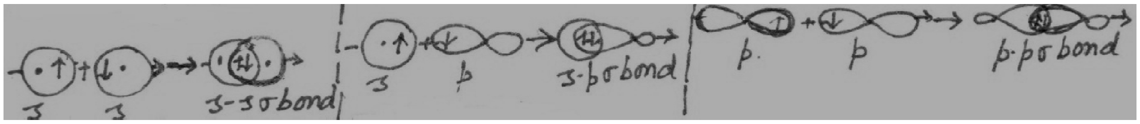
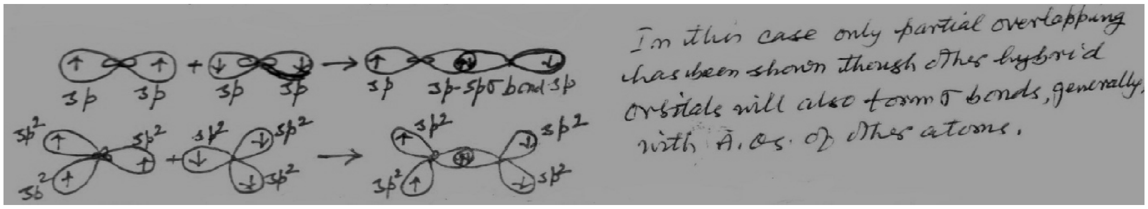


Fig 4.6(a) *formation of σbond by atomic orbitals*

(ii) Hybrid atomic orbital – hybrid atomic orbital overlapping



In this case only partial overlapping has been shown though other hybrid orbitals will also form σ bonds, generally, with A.Os. of other atoms.

Fig 4.6(b) *formation of σbond by hybrid orbitals*

In this case only partial overlapping has been shown though other hybrid orbitals will also form σ bonds, generally with atomic orbitals of other atoms.

Similarly sp^3-sp^3σ bond formation may also be shown.

π (pi) Covalent bond

A covalent bond formed between two atoms by side to side or lateral (perpendicular to the molecular axis) overlapping of only p-atomic orbitals or sometimes p and d- orbitals belonging to the valence shell of the atoms is called a π bond. If in a molecule, a particular atom uses one of its p-orbitals for σbond formation then rest of the two p-orbitals are used to form the πbonds by lateral overlapping. For example, if x axis is taken as the molecular axis, then πbond is formed by p_y - p_y or p_z-p_z overlapping as happens in the oxygen and nitrogen molecules.

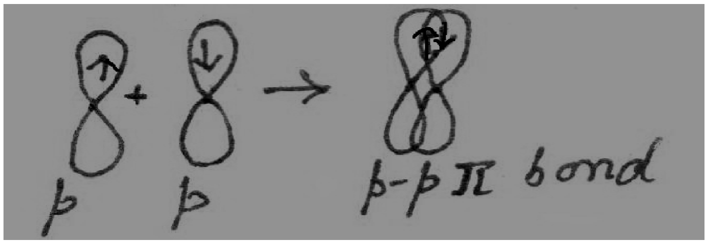


Fig 4.7 *formation of πbond by lateral overlapping of atomic orbitals*

Forσ and πbonds, the following points are important:

(i) A σbond is formed by axial overlapping of either pure or hybrid atomic orbitals of the two combining atoms while a πbond results from the lateral overlapping of the pure atomic orbitals.

(ii) A σbond is stronger than a πbond due to greater extent of overlapping of orbitals along the inter nuclear axis than in lateral overlapping.

(iii) A σbonds determine the direction of the covalent bond and bond length, πbonds have no effect on the direction of the bond. However, their presence shortens the bond length.

(iv) There is free rotation of the atoms about a σbond because the electron cloud overlaps symmetrically along the internuclear axis while this is not possible about a πbond because the electron clouds overlap above and below the plane of the atoms.

(v) A σbond has its free existence between any two atoms in a molecule while πbond is formed between the atoms only when σbond already exists.

The shapes of covalent molecules and ions can be explained by employing (a) the concept of hybridisation and (b) VSEPR Theory.

4.4. HYBRIDISATION OF ATOMIC ORBITALS

It is the theoretical model used to explain the covalent bonding in the molecules and is applied to an atom in the molecule. To explain the anomaly of expected mode of bonding (according to VBT) shown by Be, B and C in their compounds where these elements should be zerovalent, monovalent and bivalent due to the presence of 0,1 and 2 unpaired electrons in their valence shells and the observed bonding exhibited by them, i.e. these are bivalent, trivalent and tetravalent due to the availability of 2,3 and 4 unpaired electrons in their valence shells in those compounds, a hypothetical concept of hybridisation was put forward. According to this concept, before the bonding occurs in the compounds of Be, B and C, one of the 2s electrons gets promoted to the vacant 2p orbital due to the energy available from the heat of reaction when covalent bonds are formed or perhaps due to the field created by the approaching atoms, thereby making 2,3 and 4 unpaired electrons available in the valence shell of the atoms of these elements.

These orbitals having unpaired electrons then mix up together or redistribute their energy to give rise a new set of orbitals equivalent in energy, identical in shape and equal to the number of atomic orbitals mixed together. This process is known as hybridisation, the atomic orbitals are said to be hybridised and the new orbitals formed are called the hybrid orbitals. The hybrid orbitals so formed then overlap with the half filled orbitals of the approaching atoms and form covalent bonds.

Salient features (or the Rules) of hybridisation

i) The atomic orbitals belonging to the valence shell of the central atom/ion of a molecule/ion with almost similar energies mix up together or hybridise to give the hybrid obitals. But the atomic orbitals of the central atom participating in the πbond formation are excluded from the hybridisation process.

ii) The number of hybrid orbitals produced is equal to the number of atomic orbitals undergoing hybridisation. The hybrid orbitals like pure atomic orbitals can accommodate a maximum of two electrons of opposite spins.

iii) If required, electron(s) may be promoted from an orbital in ground state of the central atom to the next empty higher energy orbital provided the value of n does not change as happens in the central atom of $BeCl_2$, BCl_3, CH_4, PCl_5, SF_6etc.

iv) Most of the hybrid orbitals are equivalent in energy, shape and size but may not be identical. They differ from one another in their orientation in space.

v) From the type of hybridisation, the geometry and bond angles of a molecule can be predicted.

vi) In a few cases empty atomic orbitals or those with lone pairs of electrons (i.e. filled atomic orbitals) are also involved in the hybridisation process but in such cases normal covalent bond is not formed rather this process leads to the formation of coordinate covalent bond. Sometimes these filled hybrid orbitals do not form the bonds and the electron pair remains as lone pair on central atom.

vi. The hybrid orbitals are involved in the σbond formation only and π bond is not formed by them at all.

4.4.1. Types of hybridization:

Following are the important types of hybridisation. The central atom in a given molecule/ion can undergo any of the following possible hybridisations.

(i) Sp hybridization:

When one s and one p (oriented along molecular axis) atomic orbitals belonging to the valence shell of the central atom in a given molecule/ion mix up together to give rise two hybrid orbitals, the process is known as sp hybridisation and the new orbitals formed are called sp hybrid orbitals. This process can be shown diagrammatically as follows:

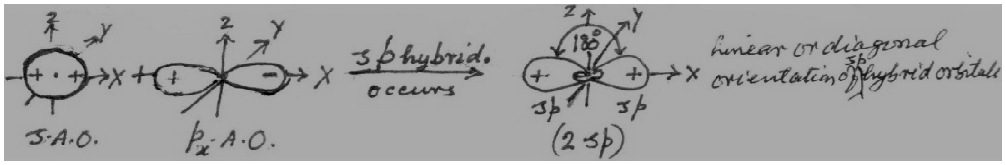


Fig 4.8 (a) *Formation of two collinear sp hybrid orbitals from the mixing of one s and one p atomic orbitals*

Characteristics:

i) These hybrid orbitals are equivalent in energy, shape (oval shaped) and are oriented in the opposite directions at an angle of 180^0 from each other, leading to linear geometry.

ii) Each hybrid orbital has one large lobe and one small lobe. The larger lobe takes part in overlapping process.

iii) These hybrid orbitals possess 50% character of s-orbital (spherical) and 50% that of p-orbital (pear shaped) and hence are oval shaped.

Examples: BeX_2 (X=H,F, Cl). Let us take BeF_2 molecule for illustration.

Be_g: $2s^2p^0$ Be_{ex}: $\longrightarrow \underbrace{2s^1p^1}_{sp}$

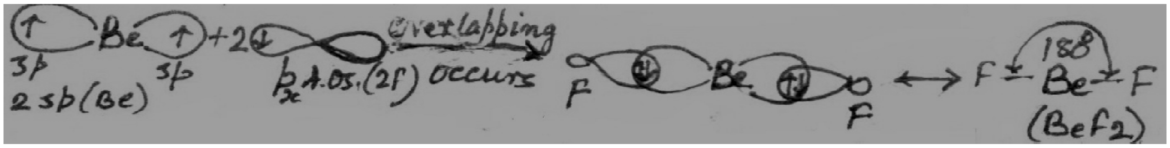


Fig 4.8 (b) *formation of two σcovalent bonds by the overlapping of sp-hybrid orbitals of Be and 2p-orbitals of F-atoms*

(ii) Sp^2 hybridisation:

On mixing together one s and any two p-orbitals belonging to the valence shell of the central atom of a given molecule/ion, a set of three hybrid orbitals is obtained. This process is known as sp^2 hybridisation and the new orbitals formed are termed as sp^2 hybrid orbitals. The process can be shown as given below:

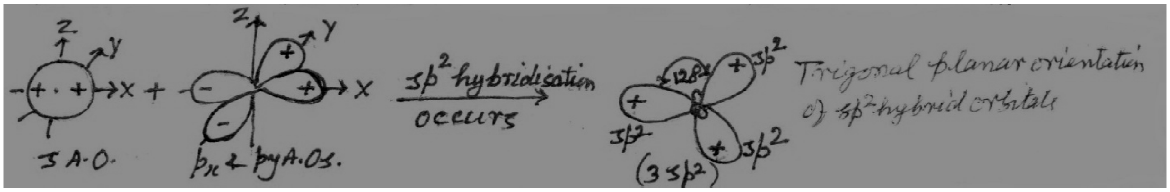


Fig **4.9(a)** *Formation of three trigonal planar sp^2 hybrid orbitals from the mixing of one s and two p atomic orbitals*

Characteristics:

i) The sp^2 hybrid orbitals are equivalent in energy and shape and are oriented towards the corners of an equilateral triangle, hence inclined at an angle of 120^{0}with one another, leading to trigonal planar geometry.

ii) They all lie in one plane (i.e. planar).

iii) They possess 33% s- character and 66% p- character and therefore are less oval than sp- hybrid orbitals.

Examples: BX_3(X=H, F,Cl) Let us take BF_3 molecule for discussion.

$$B_g : 2s^2\, 2p_x^{\ 1} \quad B_{ex}: \longrightarrow \quad \frac{2s^1 p_x^{\ 1} p_y^{\ 1}}{sp^2}$$

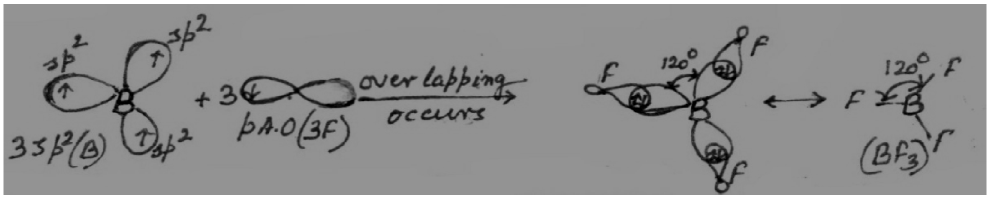


Fig 4.9(b) *formation of three σ covalent bonds by the overlapping of sp^2 hybrid orbitals of B-atoms and 2p-orbitals of 3F-atoms*

(iii) Sp^3 hybridisation:

In this hybridisation, one s and three p-atomic orbitals belonging to the valence shell of the central atom of a given molecule/ion mix up together and form a set of four hybrid orbitals. This mixing process is known as sp^3 hybridisation and the new orbitals formed are called sp^3 hybrid orbitals. This process has been shown below:

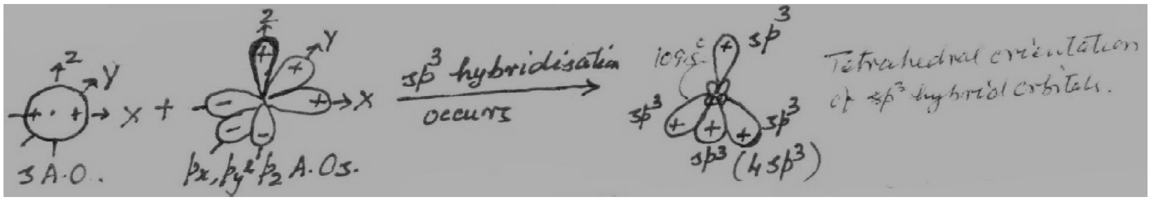


Fig 4.10(a) *formation of four tetrahedral sp^3 hybrid orbitals from the mixing of 1s and 3p atomic orbitals*

Characteristics:

i) These sp^3 hybrid orbitals are equivalent in energy and shape and are oriented along the four corners of a regular tetrahedron. The bond angle between each pair of these orbitals is 109.5^0, called tetrahedral angle.

ii) Each sp^3 hybrid orbital has 25% s- character and 75% p- character, hence their shape is closer to that of p- orbitals i.e. are pear shaped.

Examples: AX_4 where A = C, Si and X = H, F, Cl, Br, I, simplest of these is CH_4. In this molecule, C-atom is the central atom which undergoes sp^3 hybridisation as follows:

C_g:$2s^2\ p_x^1p_y^1p_z^0$ C_{ex}: $\longrightarrow$ $\underbrace{2s^1p_x^1p_y^1p_z^1}_{sp^3}$

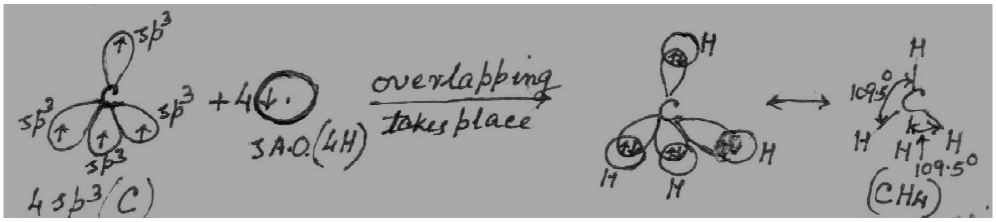


Fig 4.10 ***(b)*** *formation of four σcovalent bonds by the overlapping of* sp^3 *hybrid orbitals of C-atom and 1s orbitals of four H-atoms*

(iv) Sp³d hybridization:

When one s, three p and one d (generally dz^2) atomic orbitals of the valence shell of the central atom of a given molecule/ion mix up together and give rise to the formation of a set of five hybrid orbitals, the process is known as sp^3d hybridisation and the new orbitals formed are called sp^3d hybrid orbitals. The process of this type of hybridisation has been shown here:

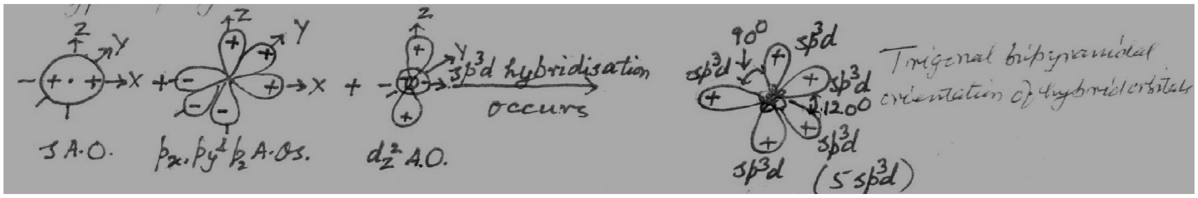


Fig 4.11 (a) *formation of five trigonal tripyramidal* sp^3d *hybrid orbitals from the mixing of one s, three p and one d* (dz^2) *atomic orbitals*

Characteristics:

i) The sp^3d hybrid orbitals are equivalent in energy and shape and are oriented towards the five corners of a regular trigonal bipyramid i.e. their spatial arrangement is trigonal bipyramidal.

ii) They do not lie in one plane. Three of the five hybrid orbitals called the basal or equatorial hybrid orbitals are oriented towards the corners of an equilateral triangle forming a triangular plane while the remaining two called axial hybrid orbitals lie above and below the plane on the axis passing through the centre of plane. The angle between each adjacent pair of basal hybrid orbitals is 120^0, that between two axial hybrid orbitals is 180^0 and that between the axial and basal hybrid orbitals is 90^0.

Examples: AX_5 molecule (A = P, As, Sb and X = F, Cl, Br). Let us discuss the hybridisation and bonding in PCl_5 molecule.

$$p_g\text{: } 3s^2\, p_x^{\ 1} p_y^{\ 1}\, p_z^{\ 1} \longrightarrow p_{ex}\text{: } \underbrace{3s^1\, p_x^{\ 1} p_y^{\ 1} p_z^{\ 1}\, d_{z2}^{\ \ 1}}_{sp^3d}$$

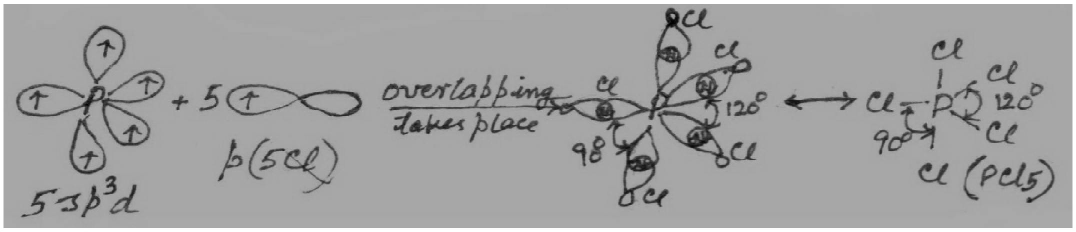


Fig 4.11(b) Formation of fiveσcovalent bonds by the overlapping of sp^3d hybrid orbitals of P central atom and p-orbitals of five Cl-atoms

(v) Sp^3d^2 hybridisation:

On mixing one s-orbital, three p-orbitals and two d (generally dx^2-y^2 and dz^2) orbitals of the valence shell of central atom of the given molecule/ion, a set of six hybrid orbitals is formed. This process is known as sp^3d^2 hybridisation and the new orbitals formed are called sp^3d^2 hybrid orbitals. The formation of these orbitals is shown below:

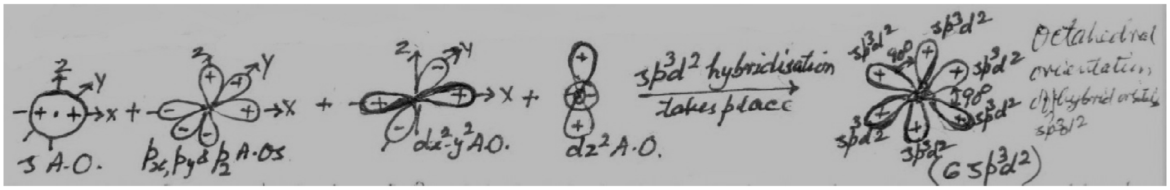


Fig 4.12(a) Formation of six sp^3d^2 hybrid orbitals from the mixing of one s, three p and two d-atomic orbitals

Characteristics:

i) All the six hybrid orbitals formed are equivalent in energy and shape and are oriented along the six corners of a regular octahedron i.e. their arrangement in space is octahedral.

ii) All the orbitals do not lie in a plane. Four hybrid orbitals of the six called basal or equatorial hybrid orbitals are lying in square plane while the remaining two called axial hybrid orbitals lie above and below the plane on the axis passing through the centre of the square base. The angles between any adjacent pairs of hybrid orbitals (basal or axial) is 90^0.

Examples: AF_6 type molecule (A=S, Se, Te). Let us see the process of bond formation in SF_6 molecule.

$$S_g: 3s^2p_x^{\,2}p_y^{\,1}p_z^{\,1} \longrightarrow S_{ex}: \underbrace{s^1p_x^{\,1}p_y^{\,1}p_z^{\,1}\,d^1_{z2}d^1_{x2-y2}}_{sp^3d^2}$$

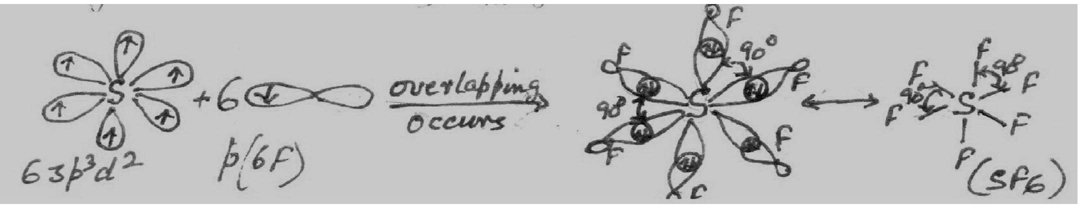


Fig 4.12 (b) *Formation of six σcovalent bonds by the overlapping of sp^3d^2 hybrid orbitals of S central atom with p-orbitals of six F atoms*

(vi) Sp^3d^3 hybridisation:

When one s, three p and three d (generally dxy, dyz, dzx) orbitals of the valence shell of the central atom in a given molecule/ion mix up together, a set of seven new orbitals is formed. This process of mixing is called sp^3d^3 hybridisation and the new orbitals formed are known as sp^3d^3hybrid orbitals. Their formation occurs as follows:

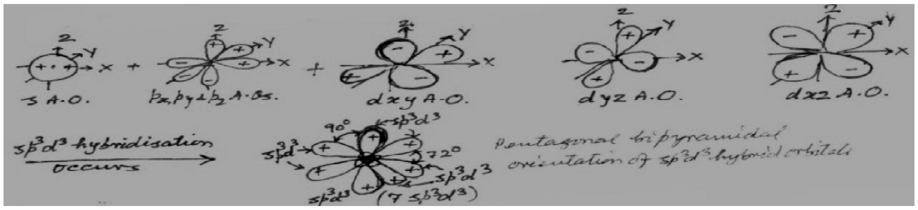


Fig 4.13 (a) *Formation of seven sp^3d^3 hybrid orbitals from the mixing of one s, three p and three d-orbitals of the central atom*

Characteristics:

i) All the seven hybrid orbitals are equivalent in energy and shape and are oriented towards the seven corners of a regular pentagonal bipyramid i.e. their spatial arrangement is pentagonal bipyramidal.

ii) All of them do not lie in one plane. Five of them lie in the pentagonal plane and are called basal or equatorial hybrid orbitals while remaining two called axial hybrid orbitals lie above and below the plane on the axis passing through the centre of the pentagonal plane.

iii) The angle between any adjacent pair of basal hybrid orbitals is of 72^0 and that between an axial and a basal hybrid orbital is equal to 90^0.

Example: IF_7 (an interhalogen compound)

$$I_g : 5s^2p_x^2p_y^2p_z^1 \longrightarrow I_{ex} : \underbrace{5s^1p_x^1p_y^1p_z^1dxy^1dyz^1dzx^1}_{sp^3d^3}$$

The whole act of hybridisation and bond formation in this molecule can be shows as given below:

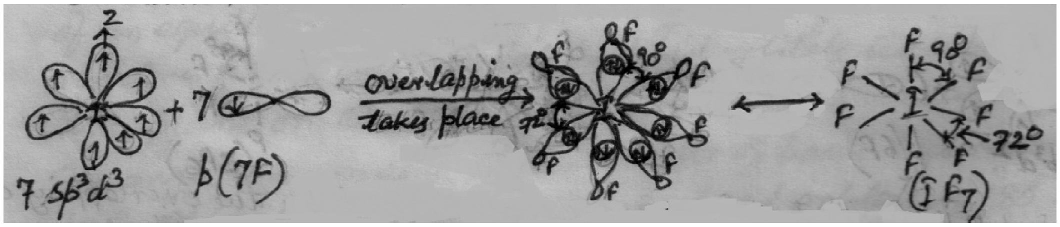


Fig 4.13(b) Formation of seven covalent bonds from the overlapping of sp^3d^3 hybrid orbitals of central I-atom and p-orbitals of seven F-atom

4.4.2 Shape of simple inorganic molecules and ions:

In all the above examples, the central atom uses all of its valence electrons for the bond formation i.e. the hybrid orbitals of the central atom and atomic orbitals (s or p) of the attached atoms are half filled, and after overlapping of the appropriate orbitals, form the normal σcovalent bonds. The molecules so formed have regular geometrical shape i.e. there is no distortion in the shape of the molecule.

However, there are examples in which the central atom of the molecule/ion undergoes a particular type of hybridisation which involves orbital/s with paired electrons as such along with orbitals having unpaired electrons. These hybrid orbitals (with both paired an unpaired electrons) overlap with the orbitals of approaching atoms to give the normal as well as dative σbonds or sometimes the hybrid orbitals with paired electrons do not overlap with the orbitals of approaching atoms and remain attached as such with the central atom in the molecules as lone pairs. The presence of these lone pairs causes distortion in the shape of the molecule/ion. This leads to irregular geometry of the molecule/ion.

The geometrical shapes, and process of hybridisation involved, of some inorganic molecule/ions along with those given under VSEPR Theory in the syllabus will be discussed after the discussion of VSEPR Theory.

4.5. VALENCE SHELL ELECTRON PAIR REPULSION (VSEPR) THEORY

The valance bond theory also called the atomic orbital theory can explain the geometrical shape of many molecules/ions of both transition and non-transition elements by employing the concept of hybridisation. But many molecules/ions remain unexplained in terms of their geometry by this method. To overcome this shortcoming, a modification of VBT was developed by Gillespie and Nyholm which can predict the shapes of many species which are left uncovered by the concept of simple hybridisation. According to this theory "The shape or the geometry of a polyatomic molecule/ion of non-transition (mostly non-metallic) element depends upon the number and nature of the electron pairs contained in the valence shell of the central atom." Thus the electrons already present in the valence shell plus the additional electrons acquired by the central atom as a result of bonding with other atoms are called its valence shell electrons. These electrons may be present as bonding or non-bonding electron pairs in the central atom which arrange themselves in such a way that there is a minimum repulsion between them and the molecule has minimum energy and maximum stability. Since there can be only one orientation of orbitals corresponding to minimum energy, hence the molecule attains a definite shape/geometry.

The following rules have been proposed by Gillespie and Nyholm to explain the shape of some inorganic molecule/ions-

i)If the central atom of a molecule/ion contains only the bond pairs of electron in the valence shell, the geometrical shape of the molecule/ion is said to be regular (or undistorted) e.g. linear, trigonal planar, tetrahedral, octahedral etc., respectively. This fact is evidenced by the examples given above in the chapter of hybridisation.

ii) When the valence shell of the central atom in a molecule/ion contains the bonding electron pairs and non-bonded electron pairs (called lone pairs), the molecule/ion has distorted or irregular geometrical shape due to the alteration in bond angles which is caused by the presence of lone pairs on the central atom.

This happens because of the following fact. Since the lone pair of electrons is under the influence of only one nucleus (of central atom), i.e. mono centric, these electrons occupy a broader orbital with a greater electron density radially distributed closer to that nucleus than bonding pair of electrons which is under the influence of two nuclei of bonded atoms i.e. bicentric. Its location between the atoms depends on the electro- negativities of the combining atoms. Thus lone pairs experience more freedom than the bonded pairs and hence exert more repulsion on any adjacent electron pair than a bond pair does on the same adjacent electron pair. The repulsion among the electron pairs follows the sequence as:

$$\underbrace{\text{l.p.-l.p. repulsion}}_{\text{maximum}}>\underbrace{\text{l.p.-b.p. repulsion}}_{\text{intermediate}}>\underbrace{\text{b.p.-b.p. repulsion}}_{\text{minimum}}$$

Because of this fact, if the central atom in a molecule/ion contains both lone pairs (l.ps.) and bonded pairs (b.ps.), there occurs a contraction in the bond angle (which is formed between two adjacent b.ps.). More the number of l.ps. on the central atom, greater is the contraction caused in the bond angle. This statement is supported by the bond angles observed in CH_4, NH_3 and H_2O:

molecules	CH_4	NH_3	H_2O
Type of hybridisation involved	sp^3	sp^3	sp^3
No. of l.ps. on the central atom	0	1	2
Bond angle	109.5^0	107.3^0	104.5^0
Contraction in the bond angle	-	$\approx 2^0$	$\approx 5^0$

iii) ∠BAB in AB_2 type molecules decreases with increasing electronegativity of the atom B where A is a central atom. This is because as the electronegativity of the attached atom B increases, the b.p. of electrons moves away from the central atom and experiences less repulsion from its l.ps. and enhanced distance between two bond pairs also causes less repulsion between them resulting in the contraction in bond angle.

For example, (i) $PI_3(\approx 102^0) > PBr_3(\approx 101.5^0) > PCl_3(\approx 100^0)$

(ii) $AsI_3(\approx 101^0) > As\ Br_3(\approx 100.5^0) > AsCl_3(\approx 98.5^0)$

iv) The repulsion between the electron pairs in filled shells is larger than that between electron pairs in incompletely filled shells. As an example, let us compare ∠HOH and ∠HSH in H_2O and H_2S molecules. It has been observed that ∠HOH (104.5^0)>>∠HSH (92.2^0). In both the molecules, the central atoms O and S contain eight electrons in their valence shells, six of their own and two from H-atoms. Thus the valence shell of O-atom (with 2s and 2p orbitals only) is completely filled but that of S-atom is incompletely filled due to the availability of 3d-orbitals (which remain vacant) in addition to 3s and 3p-orbitals. The total capacity of the valence shell of S-atom is to accommodate a maximum of 18 electrons (from $2n^2$ rule).

v) The bond angle involving the multiple bonds are generally larger than those involving only single bonds. However, the geometrical shape of the molecule is not affected by multiple bonds.

Limitations:

The VSEPR Theory suffers from certain limitations which are as follows:

(i) This theory cannot explain the shapes of very polar molecules and those having an inert pair of electrons.

(ii) The shapes of the molecules which have extensive delocalised πelectron systems are not explained by this theory.

(iii) This theory does not cover certain transition metal complexes.

The VSEPR Theory in combination with the concept of hybridisation has been successfully used to discuss and explain the geometrical shapes of most of the covalent inorganic molecules/ions. Here we shall discuss the type of hybridisation and mode of bonding in certain inorganic molecule/ions in addition to those given in the syllabus of VSEPR theory.

A. Shape of $SnCl_2$ molecule (sp^2 hybridisation)

The central atom, Sn, has the ground state valence shell configuration as given below:

Sn_g: $5s^2 5p_x^1 p_y^1 p_z^0$ → sp^2 hybridization

This atom undergoes partial hybridisation mixing up together the paired 5s and unpaired $5p_x$ and $5p_y$ -orbitals, leaving behind the empty p_z -orbital, to form three sp^2 hybrid orbitals one of which is occupied by the electron pair coming from the 5s-orbital. The process of hybridisation and overlapping of hybrid orbitals with atomic orbitals of Cl-atoms have been shown below:

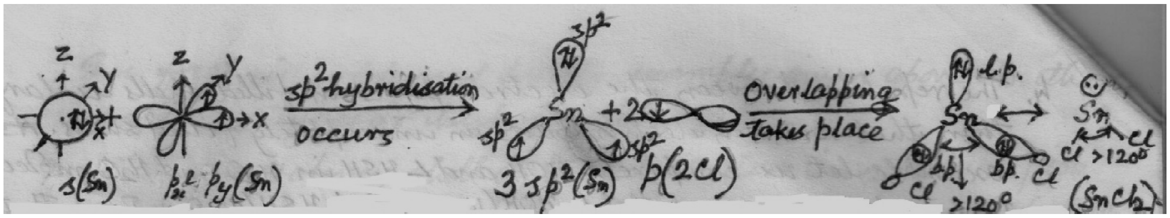


Fig 4.14 *Formation of hybrid orbitals and their overlapping with 3p-orbitals of Cl atoms to give $SnCl_2$ molecule*

Two unpaired hybrid orbitals of Sn atom overlap with unpaired p-orbitals of approaching Cl-atoms and give $SnCl_2$molecule which contains one lone pair of electrons on Sn-atom. Because of the greater repulsion of lone pair on bond pairs, the ∠Cl SnCl is less than 120^0, the expected angle in case of sp^2 hybridisation. The molecule thus attains angular or bent shape.

B. Shape of NH_3 Molecule (sp^3 hybridisation)

In NH_3 molecule, the central atom N has following ground state valence shell configuration:

N_g : $2s^2 p_x^1 p_y^1 p_z^1$ → sp^3 hybridization

All these atomic orbitals participate in hybridisation and give four equivalent sp^3 hybrid orbitals. One of them contains an electron pair (lone pair) and three half filled hybrid orbitals then overlap with 1s orbitals of three H-atoms to form σcovalent bonds (N-H bond).

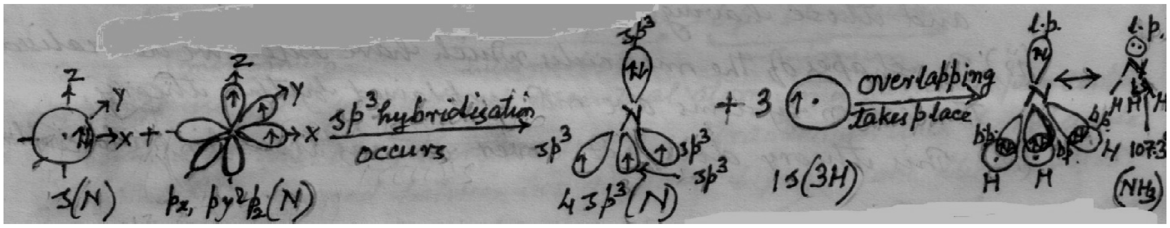


Fig 4.15 *Formation of hybrid orbitals and their overlapping with 1s orbitals of 3H atoms to give NH_3 molecule*

From the figure, it is evident that one lone pair of electrons is present in NH_3 molecule which exerts more repulsion on bonded pairs than that operating between the bonding pairs of electrons. The net result is that the NH_3 molecule attains trigonal pyramidal shape with the bond angle of 107.3^0, a deviation of about 2^0 from the tetrahedral angle of 109.5^0.

C. Shape of H_2O Molecule (sp^3 hybridisation)

The ground state valence shell configuration of the central atom O of H_2O molecule is:

O_g: $2s^2p_x^2p_y^1p_z^1$ → sp^3 hybridization

All these atomic orbitals undergo hybridisation and give rise to four equivalent sp^3 hybrid orbitals. Two of these hybrid orbitals are half filled and remaining two contain lone pairs of electrons. The unpaired hybrid orbitals than overlap with 1s orbitals of two H-atoms to form σcovalent bonds (O-H bonds).

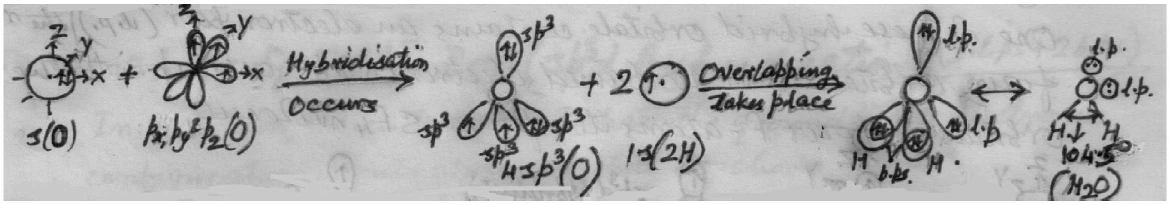


Fig 4.16 *Formation of hybrid orbitals and their overlapping with 1s orbitals of two H-atoms to give H_2O molecule*

There are two lone pairs of electrons present in H_2O molecule which exert strong repulsion on each other and move away towards the bonded pairs of electrons. This brings the bonded pairs closer to each other thereby causing contraction in the bond angle. H_2O molecule thus attains a V-shaped geometry with the bond angle of 104.5^0, a deviation of a bond 5^0 from the tetrahedral angle of 109.5^0

D. Shape of H_3O^+ Ion (sp^3 hybridisation)

Hydronium ion (H_3O^+) is formed by the combination of H_2O molecule and H^+ ion in which H_2O molecule donates one of its lone pairs of electrons to H^+ ion and it accepts that lone pair of electrons in its vacant 1s orbital.

Actually, filled sp^3 hybrid orbital of O-atom in H_2O molecule overlaps with empty s-orbital of H^+ ion as follows thereby forming a coordinate covalent bond:

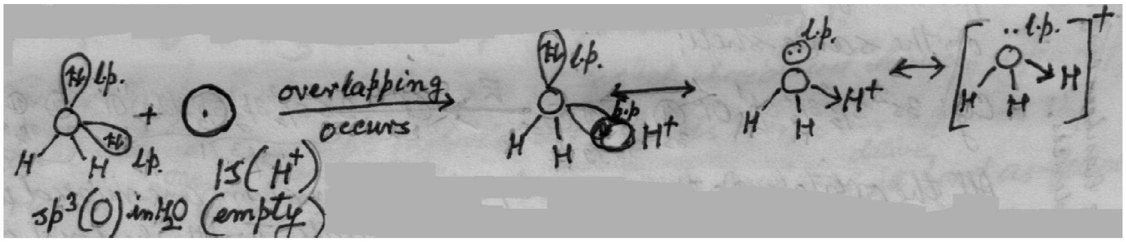


Fig 4.17 *Overlapping of filled sp^3 hybrid orbital of O-atom in H_2O and empty 1s orbital of H^+ ion to form H_3O^+ ion*

This ion has trigonal pyramidal shape like that of NH_3 molecule with one lone pair of electrons on O-atom.

E. Shape of SF_4 molecule (sp^3d hybridisation)

In this molecule the central S-atom is in its first excitation state in which one of its p_x electrons is promoted to the next empty dz^2 orbital. The electronic configuration in the ground and first excited state has been shown below:

S_g: $3s^2p_x^2p_y^1p_z^1$ $\longrightarrow$ S_{1ex} : $3s^2p_x^1p_y^1p_z^1\,(dz^2)^1$ $\longrightarrow$ sp^3d

All these atomic orbitals of S_{ex} central atom get hybridised to give five sp^3d hybrid orbitals directed toward the corners of a trigonal bipyramid, one of these hybrid orbitls contains an electron pair (b.p.) and the next four orbitals have unpaired electrons which overlap with the p-orbitals of four F-atom to form SF_4 molecule.

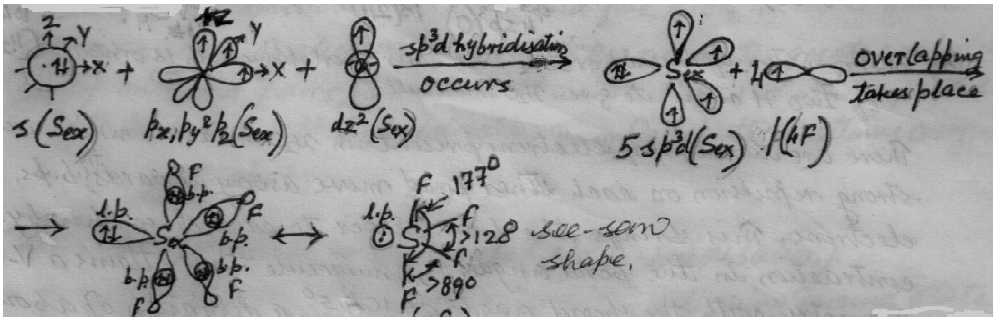


Fig 4.18 Formation of five hybrid orbitals of S_{ex} atom and their overlapping with p-orbitals of four F-atom to give SF_4 molecule

This molecule attains a see-saw shape because of the presence of one lone pair of electron (sometimes also called distorted tetrahedral) and lone pair lies at one of the basal positions (the molecule has 1 lone pair and 4 bonded pairs)

F. Shape of ClF_3 molecule (sp^3d hybridisation)

Cl is the central atom in this molecule with valence shell electronic configuration in ground and first excited state as given below wherein one electron from a filled p-orbital say p_y is promoted to a vacant d-orbital (*viz.* dz^2) of the same shell:

Cl_g: $3s^2p_x^2p_y^2p_z^1$ $\longrightarrow$ $Cl_1{}^{st}{}_{ex}$: $3s^2p_x^2p_y^1p_z^1\,(dz^2)^1$ $\longrightarrow$ sp^3d

All the orbitals of the valence shell of $C_l{}^{st}{}_{ex}$ atom are mixed up together to produce five sp^3d hybrid orbitals. Two of the hybrid orbitals have lone pairs of electrons and three have unpaired electrons which then overlap with unpaired p-orbitals of three F-atoms to form σ covalent bonds. The lone pairs are said to occupy the equilateral positions and the molecule attains T-shaped structure with the bond angle of 87.6^0 instead of 90^0 due to the distortion caused by lone pairs The T-shaped structure has been confirmed by the experimental evidences. The whole act of hybridisation, overlapping and bond formation can be shown as below (molecule has 2 lone pairs and 3 bonded pairs):

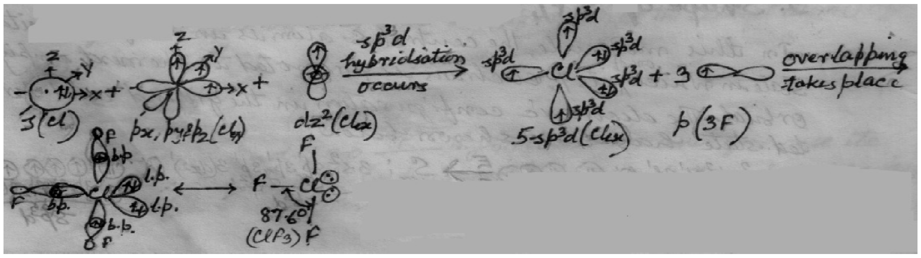


Fig 4.19 *Formation of five hybrid orbitals of $Cl_l{}^{st}{}_{ex}$ atom and their overlapping with p-orbitals of three F-atoms to give ClF_3 molecule*

The mode of hybridisation shape and bonding in BrF_3 and ICl_3 molecules can also be explained on the similar grounds as in the case of ClF_3.

G. Shape of ICl_2^- Ion (sp^3d hybridisation)

In ICl^-_2 ion, the central atom I (iodine) has the ground state electronic configuration in its valence shell as shown below:

I_g: $5s^2p_x^2p_y^2p_z^1\,(d_z{}^2)^0$

All these atomic orbitals including a vacant dz^2 orbital participate in hybridisation to produce five sp^3d hybrid orbitals of which three orbitals contain lone pairs, one hybrid orbital is half filled which overlaps with half filled p-orbitals of Cl-atom to give normal σbond and one hybrid orbital remains vacant and overlaps with the filled orbital of Cl^- ion to give a coordinate covalent σbond (dative bond). The lone pairs occupy the equatorial positions and the bonded pairs are situated in axial positions. The ion has 3 lone pairs and 2 bonded pairs as shown below and has almost linear shape:

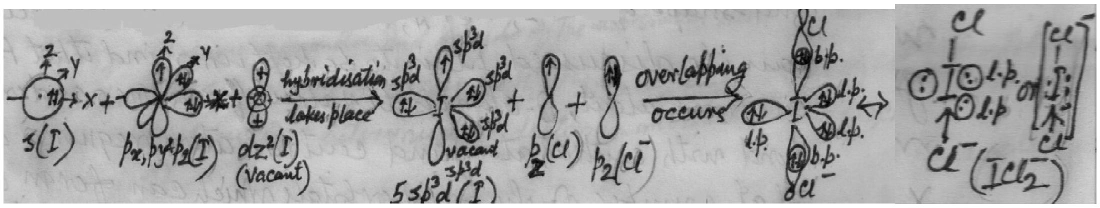


Fig 4.20 *Formation of five sp^3d hybrid orbitals ofcentral atom, I and overlapping of one of these hybrid orbitals with p-orbital of Cl atom and that of filled p-orbital* of *Cl^-ion with vacant* ***hybrid orbital of I atom***

H. Shape of NO_3^- ion (sp^2 hybridisation)

The central N-atom in this ion is sp^2 hybridised leaving a pure p_z orbital behind. These sp^2hybridised orbitals then overlap with the orbitals of one O atom and one O^-ion to form two normal σbonds and one dative σ bond as follows:

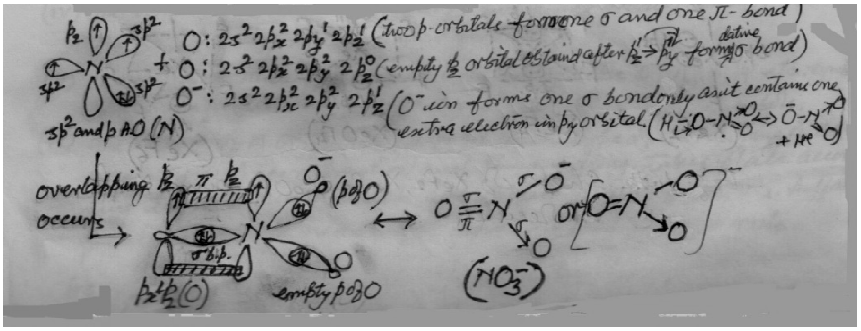
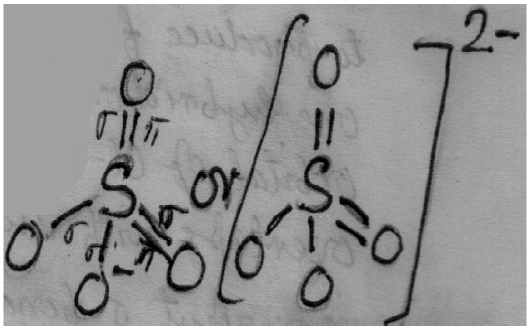


Fig 4.21 *Formation of two normalσbonds, one dative σ bond and one π bond between N central atom and oxygen atoms/ion*

I. Shape of SO_4^{2-} ion (sp^3 hybridisation)

S atom has 6 electron its valence shell and in this ion all the valence electrons of S are present in unpaired state i.e. S_{2ex} state. Out of six, four orbitals are hybridised as follows:

$S_g : 3s^2p_x^2p_y^1p_z^1 \longrightarrow S_{2^{nd}ex} : 3s^1p_x^1p_y^1p_z^1\ (d_{x2-y2})^1(d_{z2})^1 \longrightarrow sp^3$



The SO_4^{2-} ion can be shown as follows:

For details please refer to sp^3 hybridization & CH_4 molecule.

It has tetradedral shape like CH_4 molecule but has two single and two double bonds (σand π). On the similar grounds the type of hybridisation and shape of XeF_2, XeF_4, $XeOF_4$ and XeF_6 molecules can be discussed. It is to be kept in mind that F-atom is monovalent, O-atom is bivalent (forms one σand one π-bond with central atom) and central atom requires only that number of hybrid orbitals which can form σbonds with approaching atoms and these hybrid orbitals are generally unpaired or half filled. Hence in the above molecules partial hybridisation may take place.

X_eF : sp^3d 3 lone pairs + 2 bonded pairs and linear in shape

X_eF_4: sp^3d^2 2 lone pairs + 4 bonded paires and square planar

X_eOF_4 : sp^3d^2 1 lone pair + 5 bonded pairs +1 πbond and is square pyramidal

X_eF_6 : sp^3d^3 1 lone pair + 6 bonded pairs and pentagonal pyramidal

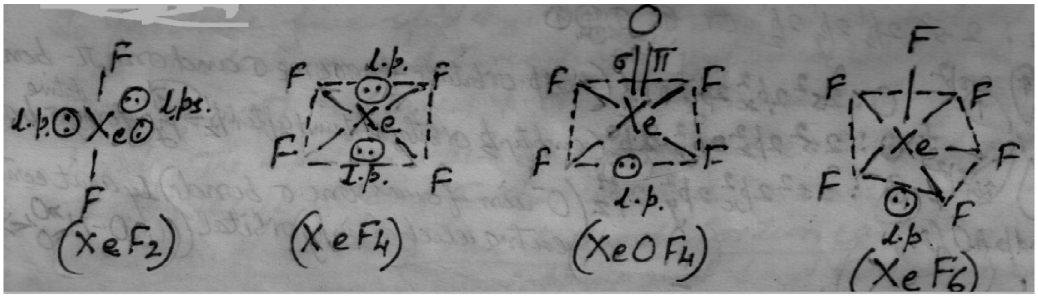


Fig 4.22 *Shapes of XeF_2, XeF_4, $XeOF_4$ and XeF_6 molecules*

4.6 MOLECULAR ORBITAL THEORY (MOT)

To explain the formation of the covalent bond in molecules/ions and their behaviour like relative bond strength, magnetic property etc., a new approach was developed by Hund and Mulliken in 1932 and later by Lennard Jones and Coulson. This approach is known as **Molecular Orbital Theory**. This theory treats the covalent bonds in terms of Molecular

Orbitals (MOs) which are associated with the entire molecule and result from the linear combination of atomic orbitals (LCAOs) of constituent atoms of the molecule/ion. Thus the molecules are supposed to have their own orbitals of varying energy in the same way as the isolated atoms have. The difference between an atomic orbital and a MO is that an electron in an atomic orbital is influenced by one nucleus only i.e. an atomic orbital is monocentric while an electron in a M.O. is under the influence of all the nuclei contained in the molecule/ion, i.e. a M.O. is polycentric.

The atomic orbitals combining linearly to form the MOs must be of the similar energy and same symmetry and may be of the two similar atoms of a homonuclear diatomic molecule/ion (e.g. H_2, H_2^+, N_2, O_2, O_2^{2-} etc.) or may be of two different atoms of a heterodiatomic molecule/ion (e.g. CO, NO, CN^-, NO^+ etc.).

The main characteristics of MOT are as follows:

(i) The atomic orbitals (AOs) combining linearly together to form the moleculer orbitals (MOs) lose their identity and the number of atomic orbitals is equal to the number of moleculer orbitals formed.

(ii) MOs are the energy states of the molecules/ions in which the electrons are filled just like in AOs of the atoms.

(iii) The linear combination of the AOs may occur in two different ways, i.e. the additive combination gives bonding molecular orbitals (BMOs) and the subtractive combination gives antibonding molecular orbitals (ABMOs).

(iv) The bonding MO has lower energy and hence greater stability than the antibonding MO obtained from two AOs.

(v) The bonding MOs are denoted by σ,π,δ,Ψetc. symbols while the antibonding MOs by $\sigma^*,\pi^*,\delta^*,\Psi^*$ etc. symbols.

(vi) The shapes of MOs formed depend on the type of combining AOs and mode of combination and their filling takes place according to the rules which are applicable for AOs, *viz*. Aufbau principle, Pauli's exclusion principle and Hund's rule of maximum multiplicity.

Formation of MOs LCAO approximation

Suppose Ψ_A and Ψ_B represent the wave function of the electrons in the A.Os. of the atoms A and B respectively. Then linear combination of these A.Os. may be done in two ways:

i) $\Psi^b = \Psi_A + \Psi_B$ (++ combination) ……… (4.10)

This additive combination of AOs gives bonding molecular orbital for which the wave function is denoted by Ψ^b. This is also called constructive interaction. Further, from the above equation, we have

$(\Psi^b)^2 = (\Psi_A+\Psi_B)^2 = \Psi_A^2+\Psi_B^2+2\Psi_A\Psi_B$ -………. (4.11)

Or $(\Psi^b)^2>\Psi_A^2+\Psi_B^2$ by a factor $2\Psi_A\Psi_B$ where squares of respective Ψs give the probability of locating the electrons in the different orbitals. From this we infer that electrons prefer to reside in the BMO rather than the AOs and placing electrons in BMO yields a stable covalent bond. In this MO the electron density is greater between the nuclei of bonding atoms.

ii) Ψ^* (or Ψ^a) = $\Psi_A-\Psi_B$ (+- (plus minus combination) ….. (4.12)

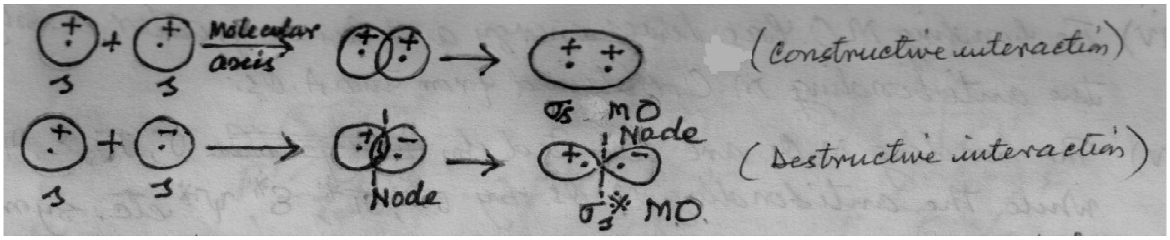
This subtractive combination of AOs gives the antibonding molecular orbital, the wave function for which is represented by Ψ^* (psi star). This is also called destructive interaction. From this equation, we have

$(\Psi^*)^2 = (\Psi_A-\Psi_B)^2 = \Psi_A^2+\Psi_B^2 - 2\Psi_A\Psi_B$ … (4.13)

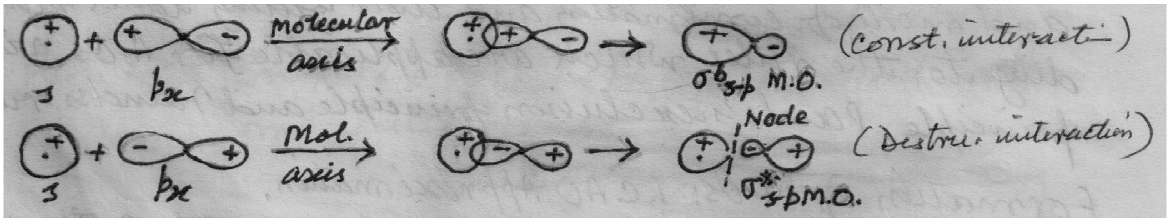
Or $(\Psi^*)^2< \Psi_A^2+\Psi_B^2$ by a factor $2\Psi_A\Psi_B$.From this relation it can be concluded that electrons prefer to occupy the AOs rather than the ABMO and placing electrons in this MO opposes the bond formation. The electron density in this MO, decreases to zero between the nuclei.

The pictorial representation of the formation of BMOs and ABMOs form AOs is shown below:

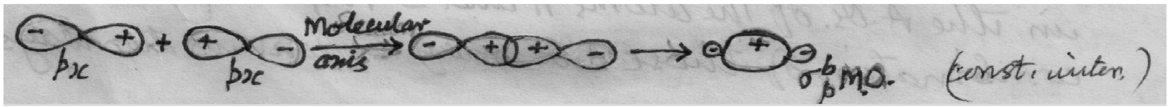
s-orbitals: combination of s-orbitals gives only σMOs (both bonding and antibonding)

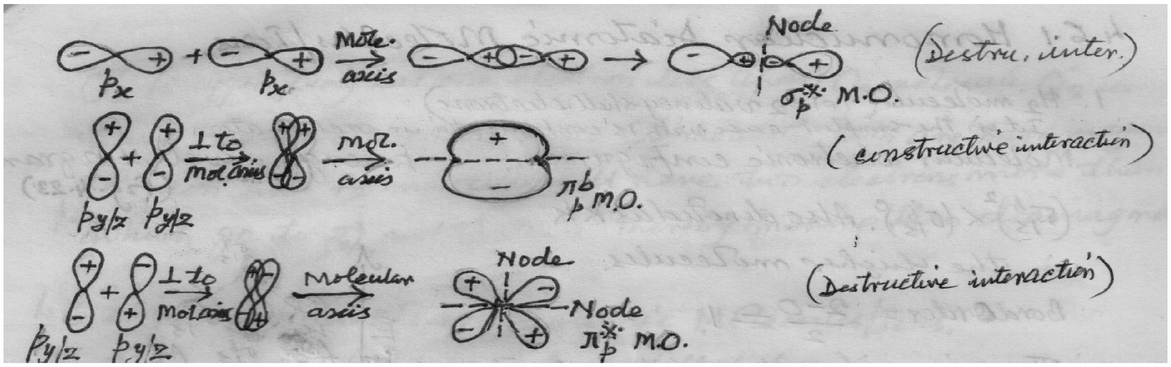


s and p-orbitals: This combination also gives only σM.Os. This is possible only along molecular axis i.e. orientation of p-orbital is along molecular axis.



p-orbitals: The linear combination of p-orbitals may give σas well as π MOs (b and * both).





It is to be noted that the interaction of AOs occurs to form the MOs only if the symmetry consideration are taken care of, e.g. s-p_x combination is allowed but s-p_y and s-Thep_z combination is disallowed if p_x lies along the molecular axis. Similarly, p_x-p_y, p_x-p_z and p_y-p_z combinations are disallowed. p_y-p_y and p_z-p_z combination will produce πM.Os. if X- axis is the molecular axis. Theπ^b_{py} and π^b_{pz} as well as π_{py}^* and π_{pz}^* MOs have the same energy, i.e. these are degenerate orbitals.

Energy level diagrams of the molecules/ions

The MOs of the molecules/ions if arranged in the increasing order of their energy, we get the so called energy level diagrams for them in which the MOs are taken as energy levels.

The electron are filled in these energy levels (MOs) from the lowest energy MO to higher energy MOs according to Aufbau principle. The degenerate MOs are filled according to Hund's rule, i.e. first singly and then in pairs. This condition is applicable to both homonuclear and heteronuclear diatomic molecules/ions.

At the same time if these MOs are written is a sequence using their symbols along with the number of electrons contained in them, then we get the molecular electronic configuration in the same way as the electronic configuration of atoms. This sequence according to increasing energy is:

$$\sigma^b_{1s} < \sigma^*_{1s} < \sigma^b_{2s} < \sigma^*_{2s} < \sigma^b_{2p_x} < \pi^b_{2p_y} = \pi^b_{2p_z} < \pi^*_{2p_y} = \pi^*_{2p_z} < \sigma^*_{2p_x}$$

This sequence has been found to hold for O_2, F_2 etc. but for hypothetical B_2, C_2, N_2 etc. $\sigma^b 2px$ is of slightly higher energy than $\pi^b 2p_{y/z}$ MOs due to certain well established reasons and hence the sequence becomes (taking x axis as the molecular axis).

$$\sigma^b_{1s} < \sigma^*_{1s} < \sigma^b_{2s} < \sigma^*_{2s} < \pi^b_{2p_y} = \pi^b_{2p_z} < \sigma^b_{2p_x} < \pi^*_{2p_y} = \pi^*_{2p_z} < \sigma^*_{2p_x}$$

Bond order: The bond order is the number of bonds in the molecular species and is given as:

Bond Order = $(N_a – N_b)/2$, N_a= number of antibonding electrons, N_b=number of bonding electrons

4.6.1. Homonuclear diatomic molecules/ions:

i) H_2 molecule (i.e. 1+1=2 valence shell electrons) It is simplest case with $1s^1$ configuration in each H-atom. Molecular electronic configuration:

$(\sigma^b_{1s})^2 < (\sigma^*_{1s})^0$. Also denoted as KK in the higher molecules.

Bond Order = (2–0)/2=1

.: There is single bond between H-atoms in H_2 molecule (H-H).

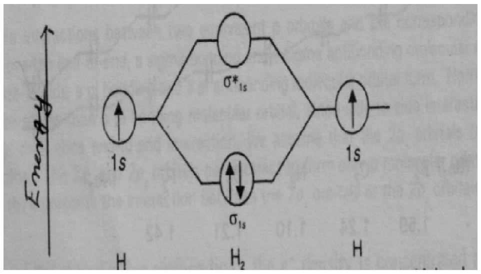


Fig 4.23) Energy level diagram of H_2

ii) N_2 molecule (5+5=10 valence shell electrons)

Each N-atom has $2s^22p^3$ electronic configuration in the valence shell. Thus Molecular electronic configuration of N_2 is:

$$(KK)^4 < (\sigma^b_{2s})^2 < (\sigma^*_{2s})^2 < (\pi^b_{2p_y} = \pi^b_{2p_z})^4 < (\sigma^b_{2p_x})^2$$

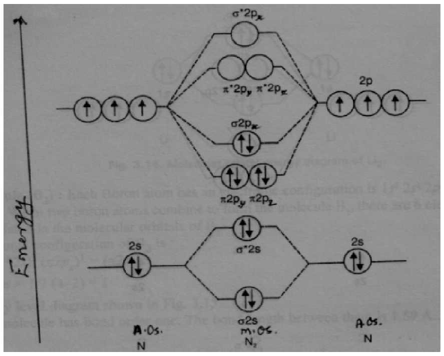


Fig 4.24 Energy level diagram of N_2

Bond order= 8-2=6/2=3. Hence there is a triple bond between N atoms in N_2 molecule. KK are non bonding orbitals.

iii) O_2 molecule (6 + 6 = 12 valence shell electrons)

Each O-atom has $2s^22p^4$ valence shell electronic configuration. $1s^2$ electrons of both O atoms belonging to KK MOs. are non-bonding.

.: Electronic configuration of O_2 molecule is**:**

$$(KK)^4 < (\sigma^b_{2s})^2 < (\sigma^{*}_{2s})^2 < (\sigma^b_{2p_x})^2 < (\pi^b_{2p_y} = \pi^b_{2p_z})^4 < (\pi^{*}_{2p_y})^1 = (\pi^{*}_{2p_z})^1$$

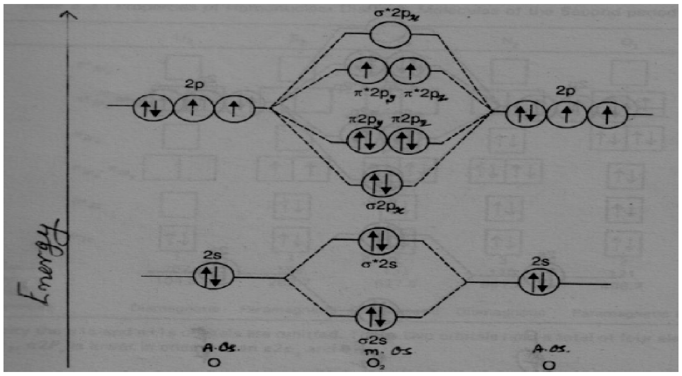


Fig 4.25 eneregy level diagrm of O2

Because of the presence of two unpaired electrons in ABMOs, O_2 molecule is paramagnetic in nature.

Bond order = (8-4)/2 = 2, There is a double bond between O-atoms in O_2 molecule (O=O)

Similarly we can write down the electronic configuration and draw the energy level diagrams for O_2^+, O_2^- (super oxide ion), O_2^{2-} (peroxide ion) and F_2 molecule.O_2^+ (oxygenyl ion) has one electron less than O_2 molecule. O_2^- ion will have one electron more than O_2 molecule. Both are paramagnetic. O_2^{2-} ion and F_2 molecule will have two electrons more than O_2 which go to π_2p_{y*} and π_2p_{z*} MOs thereby making them diamagnetic.

4.6.2. Heteronuclear diatomic molecules/ions:

i) CO molecule (4+6=10 valence shell electron).

This molecule is isoelectronic with N_2 molecule and has similar molecular electronic configuration and energy level diagram to that of N_2 molecule. There is only a minor difference in electronic distribution in A.Os. as given below:

C : $2s^22p^2$; O : $2s^2$ $2p^4$

Electronic configuration of CO molecule is (the M.O. energy level sequence is like that of N_2):

$$(KK)^4 < (\sigma^b_{2s})^2 < (\sigma^*_{2s})^2 < (\pi^b_{2p_y} = \pi^b_{2p_z})^4 < (\sigma^b_{2p_x})^2$$

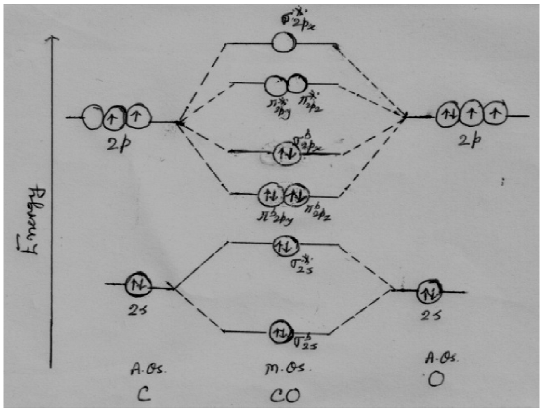


Fig 4.26 Energy level diagram of CO

Bond order =8-2/2=3 (triple bond)

ii) NO molecule (5+6=11 valence shell electron)

N: $2s^2 2p^3$ and O: $2s^2 2p^4$

The electronic configuration of NO molecule is (the M.O. energy level sequence is like that of O_2) but electron distribution is slightly different.

It is paramagnetic due to the presence of one unpaired electron. The bond between N and O is 2½ times as strong as a normal covalent bond.

Similarly, we can write down the electronic configuration and draw energy level diagram for NO^+ (one electron less than NO) ion which is diamagnetic and has only paired electrons upto $\pi^{b}{}_{z}p_{x}$ M.Os. and $\pi^{z}p^{*}{}_{y}$ M.O. is vacant.

$$(KK)^4 < (\sigma^b_{2s})^2 < (\sigma^*_{2s})^2 < (\sigma^b_{2p_x})^2 < (\pi^b_{2p_y} = \pi^b_{2p_z})^4 < (\pi^*_{2p_y})^1 = (\pi^*_{2p_z})^0$$

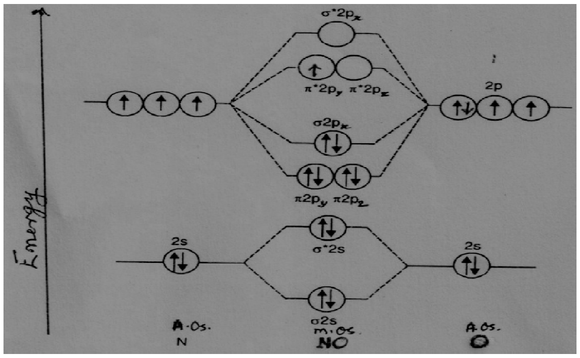


Fig. 4.27 Energy level diagram of NO

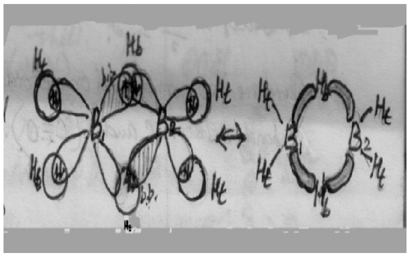
4.7. MULTICENTRE BONDING IN ELECTRON DEFICIENT MOLECULES

In the covalent compounds, in general, an electron pair bond holds two atoms together but there are a number of compounds in which an electron pair holds several atoms together. In these cases, it is said that multicentre or delocalized bond exists. The best known molecule which displays multicentre bonding is B_2H_6, diborane.

A number of evidences showthat the B_2H_6 molecule has hydrogen bridged structure in which four H-atoms are terminal hydrogen atoms (H_t) and the remaining two H-atoms are the bridging hydrogen atoms (H_b). The four H_t atoms are bonded with B-atoms by the normal electron pair bonds (two H-atoms are attached to each B-atom) and H_b-atoms form a multicentre (3c-2e) bond with each B-atom.

Boron has valence shell configuration: B_g: $2s^2p^1$ $\rightarrow B_{ex}$: $s^1p_x^1p_y^1p_z^0$ $\rightarrow$ sp^3 hybridization

Thus a maximum of three unpaired orbitals are available in B-atom to form three electron pair bonds with H-atoms to give BH_3. But the given molecule is B_2H_6, it means $H_3B?BH_3$ type situation must be there and there are no electrons available to form the B-B bond in this molecule. This anomaly has been explained as follows:



Each B-atom undergoes sp^3 hybridisation. Two of the hybrid orbitals (half filled) form two σbonds with two H_t atoms in each B-atom. Now one half filled (shaded) orbital of say $B_1$and empty hybrid orbital of B_2 overlap jointly with half filled 1s orbital of H_b atom to give $B_1H_bB_2$ type multicentre bond. Similarly, another 3c-2e bond is formed by the overlapping of empty hybrid orbital of B_1, half filled hybrid orbital (shaded) of B_2 and half filled 1s-orbital of another H_b-atom. These 3c-2e bonds are banana shaped. Therefore, this structure of B_2H_6 is also known as banana structure. Thus the H_b atoms in this molecule may be said to show bivalence which is possible only when the two H_b atoms are bonded with both the B-atoms forming two BHB bridging or 3c-2e bonds.

Another example of multicentre bonding is H_2^+ (hydrogen molecule ion) which contains a 2c-1e bond.

4.8. BOND STRENGTH

By bond strength we mean how strong is the bond between the atoms in a molecule. Bond length, bond multiplicity and extent of overlapping of atomic orbitals in addition to bond energy are the factors which determine the bond strength.

It has been observed that as the bond multiplicity increases, the bond length decreases thereby increasing the bond strength. Similarly, as the extent of overlapping between the atomic orbitals increases, the bond formed becomes stronger. That is why a σbond is stronger than a πbond. Another important factor influencing the bond strength is the bond energy(bond strength ά bond energy).

4.8.1 Bond energy:

The bond energy can be explained in two ways:

(i) Bond formation energy (ii) bond dissociation energy

(i) Bond Formation Energy:

The bond formation energy of a covalent bond A-A or A-B in a diatomic molecule A_2 or AB is the amount of energy released during the formation of these molecules from the atoms A and B.

$$\left.\begin{array}{l} \text{A+A} \longrightarrow \text{A-A + Energy released, } -E_{A\text{-}A} \\ \text{atoms} \qquad \text{molecule} \\ \text{A+B} \longrightarrow \text{A-B + Energy released,} -E_{A\text{-}B} \\ \text{atoms} \qquad \text{molecule} \end{array}\right\} \begin{array}{l} \text{these are the exothermic} \\ \text{processes, hence the} \\ \text{energy is shown with} \\ \text{negative sign} \end{array}$$

This can be defined as **"the amount of energy released when one mole (Avogadro's number) of bonds are formed between the constituent atoms in gaseous state of a molecule of A_2 or AB type".** This energy is expressed in kJ mol^{-1}.

(ii) Bond dissociation energy

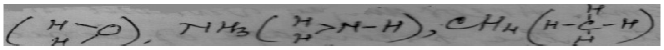
It is the energy required to break the A-A bond in A_2 or A-B bond in A-B molecule into the constituent atoms, i.e.

$$\left.\begin{array}{l} \text{A-A + Energy required, } + E_{A\text{-}A} \longrightarrow \text{A+A} \\ \text{molecule} \qquad\qquad\qquad\qquad\qquad\qquad \text{atoms} \\ \text{A-B + Energy required, } + E_{A\text{-}B} \longrightarrow \text{A+B} \\ \text{molecule} \qquad\qquad\qquad\qquad\qquad\qquad \text{atoms} \end{array}\right\}$$

these are the endothermic processes and hence the energy is shown with positive sign

This can be defined as **"the amount of energy required to break one mole of bonds in gaseous state of a molecule of A_2 or AB type into the constituent atoms."**

Evidently both the bond formation energy and bond dissociation energy for **A-A or A-B bonds** in A_2 or AB diatomic molecule are equal in magnitude but are associated with opposite processes.

In polyatomic molecules of AB_n type, n numbers of A-B covalent bonds are present e.g. H_2O etc.  molecules have two, three and four bonds respectively and equal number of bond dissociation energies are there. Each bond requires 1/n bond dissociation energy in these molecules to break up that bond.

In such cases the bond energy is actually an average bond energy. For example, there are two bonds in H_2O molecule:

$$\left.\begin{array}{lll} H_2O \quad OH+H,\ D_{HO\text{-}H} \longrightarrow & & = 496 \text{ KJ} \\ \text{and OH} \longrightarrow & O+H,\ D_{O\text{-}H} & = 426.5 \text{ KJ} \end{array}\right\}$$

Total bond dissociation energy of two covalent bond in H_2O molecule

= 496+426.5 =922.5 J mol^{-1}

The average bond energy for O-H bond in water is 461.2 kJ mol^{-1}. Thus, it can be generalized as:

Average bond dissociation energy of A-B bond in AB_n gaseous molecule

$$= \frac{\text{sum of successive A-B bond dissociation energires}}{\text{Total number of A-B bonds in } AB_n \text{ molecule (n)}}$$

4.8.2 Measurement of bond energy:

i) In diatomic molecules

The determination of bond energy in a diatomic molecule containing a covalent bond involves the measurement of heat of formation of the molecule from its free atoms. But normally this cannot be measured directly because a compound is formed from molecules and not from free atom as well as a compound on dissociation splits up into molecules and not into free atoms of its component elements. Further, a molecule cannot be completely dissociated into its free atoms merely by heating. This can, however, be obtained from heat of reaction which, in turn, is measured from the change in the degree of dissociation with temperature and from heat of sublimation.

ii) In polyatomic molecule

The average bond energy in a polyatomic molecule can be obtained from measured heats of formation and heats of atomisation. For example, to obtain the average bond energy for the C-H bond in methane, it require measurement of the heats of combustion of methane, graphite and hydrogen gas together with the heats of atomization of graphite and hydrogen gas.

4.9. PERCENTAGE OF IONIC CHARACTER

The percentage of ionic character of a polar covalent bond (also called polarity) depends on two factors: (i) dipole moment and (ii) electronegativity difference between the combining atoms. Accordingly, various methods are employed to calculate the percentage of ionic character of a covalent bond.

i) Dipole moment (dpm) method

A polar molecule acts as a dipole i.e. $A^{\delta+}$ - $B^{\delta-}$ ($\chi_A < \chi_B$) because of the electronegativity difference between the combining atoms. The degree of polarity in the molecule is given by the dipole moment (μ) which is the product of the magnitude of the charge at each centre (this is equal and of opposite in nature at the two centres) and the distance separating the two centres, i.e. positive and negative.

Thus, $\mu = q \times d$, where q is magnitude of change at each centre and d is distance between the two poles. The measured (or experimental) dipole moment (μ_{exp}) of a molecule can be used to evaluate the ionic character in a bond.

$$\%\text{ ionic character} = \frac{\text{Experimental or measured dipole moment}}{\text{calculated dipole moment (assuming 100\% ionic character}} \times 100$$

$$= \frac{\mu_{exp}}{\mu_{cal}} \times 100$$

$$= \frac{\mu_{exp}}{d_{A-B} \times \text{electronic charge}} \times 100$$

where d_{A-B} is internuclear distance between A and B atoms in AB molecule. For example, the experimental or observed dpm of HF is 1.98D and the internuclear distance (d_{H-F}) is 0.91Å. If the bond is taken 100% ionic in the molecule, then calculated dpm (μ_{cal}) is electronic charge X internuclear distance = 4.8×10^{-10} esu x 0.91×10^{-8} cm = 4.37×10^{-18} esu cm = 4.37 D (Å=10^{-8}cm and D stands for Debye)

.: % ionic character = 1.98/4.37 x100=45.3%

ii) Electronegativity difference method

In the polar molecule AB, polar covalent bond is present, the polarity or % ionic character which depends on the electronegativity difference between the linked atoms and can be evaluated by using various empirical equations.

(a) Pauling's equation

According to Pauling, the amount of ionic character in the A-B bond is:

% ionic character = 1- $e^{1/4(\chi_B-\chi_A)}$ ($\chi_B>\chi_A$)

With the help of this equation Pauling established the following relation:

χ_B-χ_A	1.0	1.7	2.0	3.0
% ionic character	ˆ22	ˆ 51	ˆ 63	ˆ 91

This shows that when χ_B-χ_A=1.7, A-B bond has 50% ionic character and 50% covalent character. When χ_B-χ_A>1.7, the bond has more ionic character than the covalent character and when χ_B-χ_A<1.7, the bond has more covalent character than ionic character.

(b) Hannay and Smith equation

These two workers proposed a more simplified equation for calculation the % ionic character in a polar covalent bond.

% ionic character = $[16\ (\chi_B-\chi_A)+3.5(\chi_B-\chi_A)^2]$ ($\chi B>\chi A$)

Using the electronegativity values as calculated by using Pauling's scale and this equation, the percent ionic character of hydrogen halide (gaseous) molecules are as follows:

HF 43%, HCl 17%, HBr 13% and HI 12%

These values reveal that the hydrogen halide molecules in gaseous state, are only partially ionic and mainly covalent.

4.10. SUMMARY

This unit of the study material consists of a concise discussion of covalent bond based on the octet rule and deviation from the octet rule. A brief account of polar and non-polar nature of covalent bond has been given. The valence bond theory and its limitations, directional nature of covalent bond as well as pictorial representation along with the formation of sigma and pi bonds have also been discussed. The concept of hybridisation has been fruitfully discussed with examples as well as shapes of inorganic molecules and ions based on hybridisation and valence shell electron pair repulsion theory have been given in the simple way.Molecular orbital theory, the energy level diagrams of the molecules/ions, multicentre bond, bond strength, bond energy and percentage of ionic character in polar covalent bonds have also been discussed and explained.

4.11. TERMINAL QUESTIONS

i) The d-orbital involved in sp^3d hybridisation is

(a) $d_z{}^2$ (b) dx^2y^2 (c) d_{xy} (d) d_{zx}

ii) Which of the following compounds contains covalent bond?

(a) NaOH (b) HCl (c) K_2S(d) LiH

iii) Which of the following compounds has the least tendency to form hydrogen bond?

(a) HF (b) NH_3 (c) HCl (d) H_2O

iv) Nitrogen atom in NH_3 molecule is sp^3 hybridised. NH_3 contains a lone pair of electron on N-atom. What is the shape of this molecule?

(a) Tetrahedral (b) square plannar

(c) Trigonal plannar (d) Trigonal pyramidal

v) Discuss the difference between a polar and a non-polar covalent bond with examples.

vi) What do you understand by directional nature of covalent bond?

vii) What is a multicentre bond. Explain with example.

viii) Discuss the shape of H_3O^+.

ix) Write down theMOelectronic configuration of O_2, $O_2{}^+$ and $O^-{}_2$and predict the bond order and magnetic behaviour.

x) Write down Hannay and Smith equation for calculating the percent ionic character of a polar covalent bond. With its help, evaluate percent ionic character present in HCl molecule (χ_H= 2.1, χ_{Cl}=3.0).

xi) Draw molecular orbital energy level diagram for NO^+ ion and predict its magnetic behaviour.

xii) XeF_2 molecule is linear though Xe atom in this molecule undergoes sp^3d hybridisation. Explain.

4.12. ANSWERS

i) (a)

ii) (b)

iii) (c)

iv) (d)

v) Please see polar and non-polar covalent bonds

vi) Please refer to directional characteristics of covalent bond

vii) Please refer to multicentre bonding

viii) Please see the VSEPR Theory

ix) Please see the MO theory

x) please refer to % ionic character of polar bond

xi) Please see the MO theory

xii) Please refer to shapes of inorganic molecules

4.13 . REFERENCES

For references and list of books consulted kindly see at the end of Unit 5.

UNIT 5 : CHEMICAL BONDING II

CONTENTS:

5.1. OBJECTIVE

The objective of writing the study material of this unit is to make the readers comfortable with electrostatic attraction forces and to acquaint them with the exciting world of the ionic crystals. An attempt has been made to through light on the type of force that holds an extremely large number of ions together forming a bulk or cluster of ions which exists in solid state only. At the same time the text gives an idea about why are the ions in an ionic crystal arranged in a regular manner and have a definite ratio. It has also been tried to give a brief account of lattice defects and semi conductors which are of immense importance industrially. The readers must also have an idea of the covalent character of ionic bond and weak interactions which has been taken care of.

5.2. INTRODUCTION

The solids have been classified in two different ways:

A. First kind of Classification

This classification gives two categories of solids, *viz.* true solids and pseudosolids.

(i) True solids-These have definite shape and volume which are retained even on long standing. These are rigid and hence cannot be distorted. These solids have sharp melting points. Examples are NaCl, KCl, Fe, Cu, S etc.

(ii) Pseudo solids-These do not have definite shape and volume and lose them on long standing. These are less rigid and hence can easily be distorted. These solids melt over a range of temperature. Examples are glass and pitch.

B. Second kind of classification

This classification is more appropriate and gives three categories of solids, *viz.* crystalline solids, non-crystalline or amorphous solids and polycrystalline solids.

(i) Crystalline solids- The constituent particles (atoms, ions or molecules) of these solids are arranged in a regular and definite manner in three dimensional space. These are said to have long range order. They have sharp melting points and can be broken into pieces, e.g. NaCl, sugar, diamond, graphite, sulphur etc.

(ii) Amorphous solids- The constituent particles of these solids are not arranged in a regular manner and hence have short range order. These do not have sharp melting points, i.e. they first soften and then change to liquid state on heating. Example are glass, rubber, plastics, silica etc.

(iii)Polycrystalline solids- These solids occur as powder and resemble amorphous solids but their individual particles have all the characteristics of crystalline solids.

Based on the nature of bonding forces existing between the constituent particles of crystalline solids, these have further been categorised into five classes, *viz.* ionic crystals, covalent crystals, molecular (van der Waals') crystals, metallic crystals and hydrogen bonded crystals.

Lattice points and crystal lattice

It has been mentioned above that the constituent particles of a crystalline solid are arranged in a regular order. The position of these particles relative to one another in the solid is represented by points (·) which are called lattice points or lattice sites and the orderly arrangement of these infinite lattice points is called a crystal lattice or space lattice.

Unit cell is a small unit of lattice points which on repeating infinitely in three dimensions gives a crystal lattice. This small unit is called a unit cell of the lattice. This shows all the properties of the crystal lattice.

5.3 IONIC SOLIDS

In these solids, the constituent particles are the ions, both positive and negative, which are held together by strong electrostatic force of attraction. There operates a repulsive force between the ions of same charge if these are adjacent to each other, therefore, the ions of similar charge move away from one another and those of opposite charge come closer together. These ions are arranged in the crystal lattice in regular pattern where the positive ions are surrounded by a definite number of negative ions and the negative ions, in turn, are surrounded by a certain number of positive ions. The attractive forces are maximum when each ion is surrounded by the greatest possible number of the oppositely charged ions. The positive and negative ions are present in the crystal lattice in a simple whole number ratio, i.e. 1:1, 1:2, 2:1 etc. The ionic solids along with other crystalline solids have been assigned seven basic crystal systems. These systems along with types of space lattices present in the crystal system and examples have been given below (**Table 5.1**):

Table. 5.1 The seven crystal systems

S. No.	**Name of the crystal system**	**Type of space lattices present in the crystal system**	**Examples**
1	Cubic	(i) Simple cubic (SC) (ii) Body-centred cubic (BCC) (iii) Face- centred cubic	NaCl, KCl, CaF_2, $NaClO_2$ ZnS, Cu_2O, alums, diamond Pb, Au, Ag, Hg

		(FCC)	
2	Orthorhombic	(i) Simple orthorhombic (ii) Body centred orthorhombic (iii) End – centred orthorhombic	KNO_3, K_2SO_4, $BaSO_4$, $MgSO_4$ Mg_2SiO_4 Pb CO_3, α–sulphur.
3	Tetragonal	Simple tetragonal Body centred tetragonal	$NiSO_4$, SnO_2, TiO_2 $ZrSiO_4$, KH_2PO_4, $PbWO_4$
4	Monoclinic	Simple monoclinic End-centred monoclinic	Na_2 SO_4. 10 H_2O FeO_4, $CuSO_4$. $2H_2O$, $Na_2B_4O_7$. $10H_2O$
5	Triclinic	Simple triclinic	$CuSO_4.5H_2O$, $K_2Cr_7O_7$, H_3BO_3
6	Hexagonal	Simple hexagonal	AgI, ZnO, CdS, HgS, PbI_2, quartz, Mg, Cd, Zn.
7	Rhombohedral	Simple	$NaNO_3$, calcite, magnesite, Sb, Bi.

The ions in a given ionic crystal are arranged (or packed) in different ways which are given below:

(i) **Hexagonal close-packed** (hcp) **structure,** i.e. AB AB ………packing of spheres.
This structure has the packing sequence of different layers of spheres as AB AB….. In this structure, each sphere is surrounded by 12 other nearest spheres and hence the coordination number (CN) of each spheres is 12.

(ii) **Cubic close-packed** (ccp) **or face-centred cubic** (fcc) **structure,** i.e. ABC ABC……packing of spheres.

This structure has the packing sequence of different layers of spheres is ABC ABC………This structure has cubic symmetry. Each sphere is surrounded by 12 other nearest spheres in this arrangement and hence the coordination number of each sphere is 12.

In both of the above structures, the coordination number of each sphere is 12 since each sphere is surrounded by six nearest spheres lying in the same layer, three spheres lying in the layer just above it and three spheres lying in the layer just below it. Both types of the above structures have the same packing efficiency which is 74 %, i.e. 74 % of the total volume of the unit cell is occupied by the spheres.

(iii)**Body-centred cubic** (bcc) **structure-**In this arrangement, there are 8 spheres at eight corners of a cube and one sphere at the centre of the cube. Each sphere is in contact with 8 other spheres in this structure and hence the coordination number of each sphere is 8.

Interstitial sites (holes or voids) **in ionic crystals**

In an ionic crystal, the bigger ions (i.e. anions) have close packed structure which may be either hexagonal close packed or cubic close packed type. In this close-packed structure, there is some vacant space between the anions which is called interstitial site (or hole or void). These sites or voids are occupied by smaller ions, i.e. cations.

Depending on the number of anions and the pattern in which they surround a cation in a given ionic crystal, there are four types of interstitial sites, *viz.* trigonal (C.N. = 3), tetrahedral (C.N. =4), octahedral (C.N. =6) and cubic (C.N. =8), respectively.

5.3.1 Characteristics of ionic solids:

Following are the main characteristics of ionic solids:

(i) The constituent particles of these solids are the cations and the anions which are held together by strong electrostatic force of attraction known as ionic bond and these exist as crystalline solids.

(ii) The ionic bond in ionic crystals is not rigid and nondirectional, i.e. it extends equally in all directions. Hence the ionic solids neither have any definite geometry nor show stereoisomerism like covalent molecules.

(iii)Since the anions are generally larger in size than the cations, the anions have closest packing arrangement in ionic solids in which there are left some empty spaces called interstitial sites or voids. These sites may be tetrahedral, octahedral or cubic type which are occupied by the cations.

(iv) Each ionic solid is formed from a small unit called a unit cell which contains a definite number of cations and anions. This unit cell in electrically neutral.

(v) The ionic solids are poor or bad conductors of electricity because in solid state the ions are fixed in their position and cannot move even if an external electric field is applied on them. However, in fused state or in aqueous solution they conduct electricity because under these conditions the ions are free to move. Also, the ionic solids having defects can conduct electricity due to the movement of ions from the lattice sites to the vacancies or that of free electrons present in them.

(vi) These solids are very hard and brittle due to the movement of one layer over the other along a plane on applying external force.

(vii) These have lattice energy and high melting points and boiling points.

(viii) These solids are generally soluble in water or polar solvents due to ionization and undergo ionic reactions in that medium.

5.3.2 Crystal coordination number (CCN):

We have learnt above that in ionic crystals the positive ions are surrounded by a definite number of negative ions and vice versa. The number of ions of opposite charge surrounding an ion in the ionic crystal is called the crystal coordination number or simply coordination number (C.N.)

In case of ionic crystals of AB type (e.g. NaCl, CsCl, Zns etc.) in which the number of both kind of ions is same, the C.N. of cation is equal to the C.N. of the negative ion, e.g. in NaCl crystal each Na^+ ion is surrounded by six equidistant Cl^- ions and each Cl^- ion, in turn, is surrounded by six equidistant Na^+ ions. Hence the coordination number of both Na^+ and Cl^- ions is 6. In CsCl, the C.N. of Cs^+ ion and Cl^- ion, both is 8 (due to different type of packing of ions than in NaCl).

In ionic crystals of the type AB_2 or A_2B (e.g. CaF_2, Na_2S etc.) in which the cation-anion ratio is 1:2 or 2:1, the two types of ions have different coordination numbers. For example, in Ca F_2, the C.N. of F^- ions is half to that of Ca^{2+} ions. The X-ray study has shown that C.N. of Ca^{2+} ions is 8 and that of F^- ions is 4.

5.3.3 Radius ratio (R_r):

In an ionic crystal, the arrangement of ions (packing) and their coordination number depend on the relative size of ions or the ratio of radii of the ions which is known as radius ratio. Thus the radius ratio (R_r) is defined as "**the ratio of the radius of cation (r_{C+}) to that of anion (r_{A}-) in an ionic crystal**". This can also be shown as

$R_r = \frac{r_{C+}}{r_{A-}}$ Where $r_{C+}$is the radiusof cation and r_A-is the radius of anion, R_r is radius ratio.

The radius ratio plays an important role in determining the structure of ionic solids and predicting the coordination number of the cation or the anion.

Radius ratio effect

The effect of radius ratio in determining the coordination number and the arrangement of ions (structure or packing) in an ionic crystal is known as radius ratio effect. As the cation becomes larger with respect to the anion, i.e. R_r increases, higher number of anions can fit around the cation and hence the coordination number of the cation increases. Which C.N. will give the most stable arrangement of ions is dependent on radius ratio.

The relationship between the various ionic arrangements and the radius ratios is given below:

Limiting value of $\frac{r_{c+}}{r_{A-}}$	Coordination number	Arrangement of ions
< 0.155	2	Linear
0.155-0.225	3	Trigonal planar (B_2O_3)
0.225-0.414	4	Tetrahedral (ZnS)
0.414-0.732	4	Square planar
0.414-0.732	6	Octahedral (NaCl)
0.732-0.999	8	Body centred cubic (CsCl, CaF_2)

The R_r value can be used for predicting the ionic arrangement and C.N. in the ionic crystals as already mentioned. For example, the radius ratio for NaCl crystal is r_{Na+}/r_{Cl}-= 0.95Å/1.81Å = 0.525. This value lies between 0.414 and 0.732. Thus the C.N. should be either 4 or 6 and the arrangement should be square planar or octahedral. The X- ray study of NaCl crystal has revealed that the crystal has octahedral arrangement of ions, i.e. each Na^+ ion is surrounded by six equidistant Cl^- ions and each Cl^- ion has six equidistant Na^+ ions. The cation-anion stoichiometry is 1:1 and the C.N. is 6 for both the ions. Similarly, it can be shown for CsCl (R_r = 169/181 = 0.93) that the C.N. is 8 for both the ions and arrangement of ions in the crystal is cubic.

Let us now consider the effect of R_r on the C.N. of the ionic crystal:

(i) If the value of R_r decreases due to decreasing size of cation or increasing size of anion, the crystal will become unstable. In this arrangement all the anions will not be able to touch the outer surface of cation. To do so, anions will move closer to each other and repulsion between them will increase. This repulsion pushes away one or more anions so that remaining anions fit around the cation giving more stable arrangement and coordination number may decrease from 8 to 6 or from 6 to 4.

(ii) It R_r increases either by increasing cationic size or decreasing anionic size, the arrangement will not be stable. In such a case the outer surfaces of the anions will not touch each other. On further increasing the R_r value, anions move far apart from each other and more anions may be accommodated in the packing arrangement. As a result, the coordination number may increase from 4 to 6 or from 6 to 8 This happens with Cl^- ion in NaCl (C.N. 6) and CsCl (C.N. 8).

5.3.4 Limitations of R_r rule:

Though the radius ratio rule is applicable to a majority number of ionic crystals, yet there are exceptions also. Following are some limitations of this rule:

(i) The ionic radii measured are not accurate or reliable because the radius of an ion is not constant but changes depending on its environment. It has been observed that the radius of an ion increase about 3% when C.N. changes from 6 to 8 and decreases about 6% when C.N. changes from 6 to 4. In such cases the radius ratio rule does not apply.

(ii) The R_r rule is valid to the packing of hard spheres of known size only. The anions are not hard due to their large size and are polarisable under the influence of cations thereby forming covalent bonds which are directional in nature and may prefer other orientations.

(iii) This rule does not explain the octahedral lattice arrangement of oxides of large divalent cations such as Pb^{2+}, Sr^{2+},Ba^{2+} etc. through they are expected to have this arrangement (structure).

(iv) Rb halides (RbX,X = Cl, Br, I) show C.N. 6 at ordinary conditions but adopt the CsCl structure at high pressure. Rr rule is unable to explain this observation.

(v) According to this rule, Li-halides should adopt 4-coordination structure but they crystallize in octahedral lattice thus violating the R_r rule. It may be due to covalent character of halides of lithium.

5.4 LATTICE DEFECTS

The packing of ions (or structure) in the ionic solids given above relate to ideal crystals. An ideal crystal is that which has the same unit cells containing the same lattice points throughout the whole of the crystal.

At absolute zero, most of the ionic crystals show well-ordered arrangement of ions and there are no defects, if the crystals are ideal. With rise in temperature, however, there is a chance that one or more of the lattice sites may remain unoccupied due to the migration of ions from their positions to the interstitial sites or out of the surface of the crystal. This constitutes a defect called lattice or point defect. The lattice defects in the ionic crystals are of three types:

(i) Stoichiometric defects
(ii) Non-stoichiometric defects
(iii) Impurity defects

(i) Stoichiometric defects

In the stoichiometric crystals of the compounds, the ratio of different atoms or ions is exactly the same as indicated by the chemical formulae of the compounds. These compounds obey the law of constant composition. If there is deviation from this ideal or perfect crystal structure, the crystal is said to have the defect or imperfection which arises due to the presence of cationic or anionic vacancies or dislocation of ions in the lattice structure. Accordingly, these defects are of two types:

(A) Schottky defects

If equal number of cations and anions are missing from their lattice sites in an ionic crystal of the type A^+B^- and the electrical neutrality of the crystal is maintained, the resulting defect is called the Schottky defect. This consists of pair (s) of holes in the crystal lattice due to missing cation (s) and anion (s).

This type of defect occurs mainly in the highly ionic compounds where

(i) The cations and anions are of similar sizes

(ii) C. N. of the ions is high, i.e. 6 or 8

Examples: NaCl, KCl, CsCl etc.

The presence of this defect decreases the density of the crystal due to missing ions.

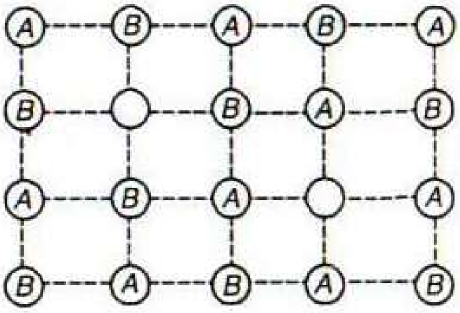


Fig. 5.1 Schottky defect showing one cation and one anion missing

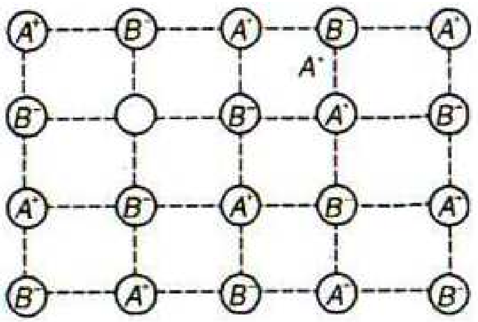


Fig. 5.2 Frenkel defect showing migration of cation to interstitial site

(B) Frenkel defects

This type of defect arises in the ionic crystals due to the departure (or migration) of an ion, usually cation due to its smaller size, from its regular position in the lattice to the vacant interstitial site between the lattice points. This creates a hole in the lattice. The electrical neutrality and the stoichiometry of the crystal are maintained even after this defect is created. This defect occurs mainly in the compounds where;

(i) There is large difference in the cationic and anionic sizes, i.e. an ions are much larger in size than cations (R_r is low)

(ii) The C.N. of the ions is low, i.e. 4 or 6

Examples: ZnS, AgCl, AgBr, AgI etc.

Lattice vacancies (or holes) occur in almost all the ionic solids. However, Schotlky defect occurs more often than Frenkel defect. The reason being much less energy required to form a Schottky defect than needed to create a Frenkel defect. X-ray diffraction of Nacl crystal has shown that at room temp., this substance has one defect for 10^{15} lattice sites but at 500^0C 10^9 defects and at 800^0C, 10^{11} defects have been observed for the same number of lattice sites.

Consequences of the stoichiometric defects

(i) Crystalline solids having these defects are able to conduct electricity to a small extent when an electric field is applied on them. This happens through an ionic mechanism, i.e. a nearby ion under the influence of electric field moves from its lattice site to occupy the vacancy present in the crystal and creates a new hole. Another nearby ion moves to occupy this vacancy. The process in repeated many times thereby causing a hole to migrate across the crystal which is equivalent to moving a charge in the opposite direction. In alkali halides, the migration of cation only has been detected below 500^{0}c but both ions migrate at higher temperature thereby increasing the conduction.

(ii) The presence of holes lowers the lattice energy and hence the stability of the crystal. If too many holes are present, then it may cause a partial collapse of the lattice.

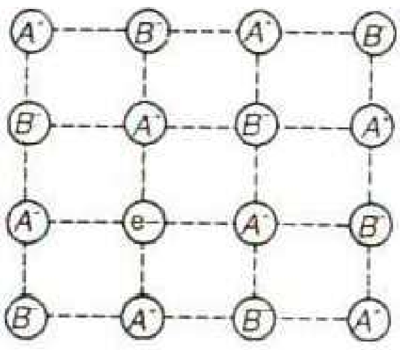
(iii)The closeness of similar charges brought about by the Frenkel defect tends to increase the dielectric constant of the crystals.

(ii) Non-stoichiomstric defects

In the non-stoichiometric crystals, the ratio of different atoms or ions present in the compound differs from that which is required by ideal chemical formula of the compound. These compounds do not obey the law of constant composition. In such cases, there is either an excess of metal ions or deficiency of metal ions (or excess of anions) which creates non-stoichiometric defect. The crystal as a whole is neutral but the crystal structure becomes irregular. These defects can exist in a crystal in addition to the stoichiometric defects. These defects are of two types:

(a) Metal excess defects

In these defects the positive ions are in excess. These may arise due to either the absence of anions, i.e. the anions are missing from the lattice sites leaving the vacancies which are occupied by extra electrons to maintain the electrical neutrality or due to the presence of extra cations occupying the vacant interstitial sites in the lattice which are counter balanced by extra electrons also present in interstitial space.



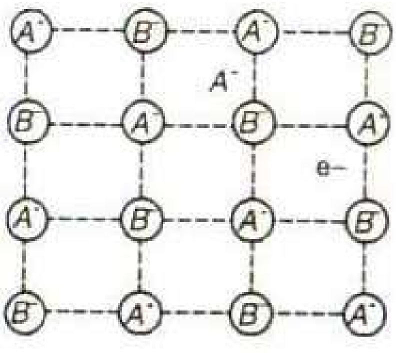


Fig. 5.3 (a) Metal excess defect due to missing of anion Fig. 5.3 (b) Metal exess defect due to interstitial cation

The anion sites occupied by electrons are called F-centres which are responsible for the colour of the compounds and their paramagnetic behaviour. The first type of metal excess defect is produced by heating the compound with excess of metal vapours. Examples: NaCl, KCl etc. The second type defect is observed in ZnO, CdO, Fe_2O_3, Cr_2O_3 etc.

(b) Metal deficiency defects

These defects occur in the compounds where the metal ion exhibits variable oxidation state, i.e. the compounds of transition elements. The defect is caused either due to missing cations from the regular positions in the lattice thus creating cation vacancies and to maintain the electrical neutrality, the nearby cations acquire extra positive charge (examples FeS, FeO, NiO etc.) or the defect may also be produced by the presence of extra anions in the interstitial sites. The extra negative charge is balanced by extrapositive charge on some of the cations. However, due to the larger size of anions, these can hardly be adjusted in the interstitial sites. Therefore, the examples of this type of defect are rare and the defect remains merely a theoretical possibility.

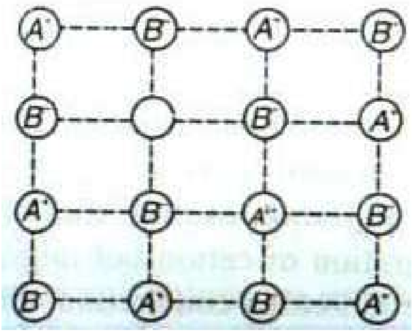


Fig. 5.4 (a) Metal deficiency defect due to missing cation

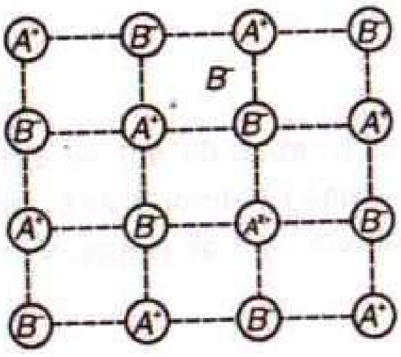


Fig. 5.4 (b) Metal deficiency defect due to an interstitial anion

Consequences of non-stoichiomtiric defects

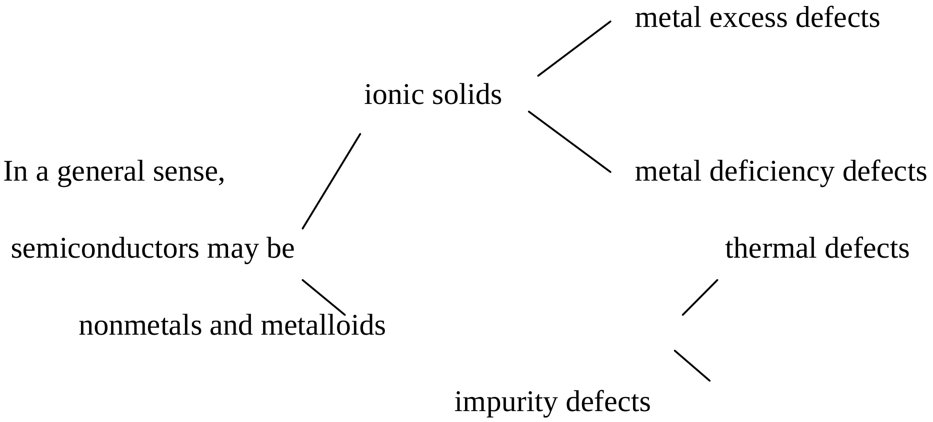
Due to the metal excess defects the compounds show electrical conductivity because free electrons present in the crystals can migrate easily under the electric field. Since the number of defects and hence the number of electrons is small, so such compounds show lesser conductance than metals, fused salts or dissolved salts. These compounds, therefore, are termed as semiconductors. These electrons may also be excited to higher energy levels by absorption of certain wavelengths from the white light (visible range) and are responsible for colour of the compounds.

The crystals of the compounds with metal deficiency defects can also act as semiconductors due to the movement of electrons from one ion of normal oxidation state to that of higher oxidation state to create another higher oxidation at its position. This type of movement of electrons between the ions appears as an apparent movement of positive holes thereby making the crystal a semiconductor.

5.5 SEMICONDUCTORS (THERMAL DEFECTS AND IMPURITY DEFECTS)

Semiconductors are the materials which have electrical conductivity at normal temperature which isintermediate between a conductor (like metals) and an insulator. Thus, the semiconductors allow only a portion of the applied electric field to flow through them. According to the band theory which differentiates among conductors, semiconductors and insulators, the semiconductors are the solids which have only a small difference of energy between the filled valence band of electrons and an empty conduction band. This is called band gap. If this band gap can be overcome by any means, *viz.* thermal energy or impurity addition, the electrons from the filled band may go to higher energy empty conduction band in a limited number thereby making the material to conduct electric current.

This is evident from the fact that there are some materials which may be insulators at low temperature, (i.e. absolute zero) but become conductors at elevated temperatures (thermal defects) or on adding certain impurities (impurity defects). These are called semiconductors, e.g. crystals of silicon (Si) and germanium (Ge).



The conductivity of the semiconductors arises in the following two ways:

(i) **Intrinsic semiconductors (thermal defects)**

A semiconductor which is obtained by heating an insulator is called intrinsic semiconductor, i.e. the defect in the crystal is produced by thermal energy. Pure silicon, pure germanium or pure grey tin are some examples of materials which act as semiconductors. Actually at elevated temperatures, sufficient amount of energy is available to break the covalent bonds in the crystal to make some electrons free. These electrons can migrate through the crystal leaving behind positive holes at the site of missing bonds. We can thus conclude that the heat energy promotes some electrons from the filled band into the next higher energy conduction band across the small energy gap and the material becomes conductor. With the rise in temperature the conductivity of semiconductors, therefore, increases.

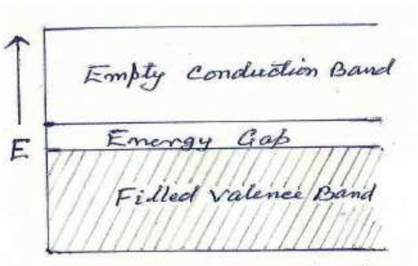


Fig5.5 Energy bands in a semiconductor

Fig. 5.5 Energy bands in semiconductor

(ii) **Extrinsic semiconductors (impurity defects); n-type and p-type semiconductors**

Certain defects in crystals arise from the presence of chemical impurities called impurity defects. Thus the materials obtained by adding impurity atoms to the insulators and making them conductors are called extrinsic semiconductors which are said to have impurity defects. For example, the addition of phosphorus, arsenic, boron or gallium atoms to silicon or germanium crystals makes them semiconductors. These are of two types:

(a) **n- type semiconductors (n = normal)**

If a very small amount of (say) arsenic, the element of group 15th,is added as impurity to the pure crystal of silicon, the element of group 14, by a suitable means, the process is called doping and we get the so called arsenic dopedsilicon. During the process of doping, a minute proposition of Si atoms is randomly replaced by arsenic atoms with one extra electron in their outer shell because only four outer electrons of As are required to form bonds with neighbouring Si atoms in the lattice (Si, ns^2p^2& As: ns^2p^3, i.e. Si has 4 and As has 5 valence electrons). At low temp., like absolute zero, these free electrons are located at the As atoms but at normal or elevated temperatures, these free electrons migrate through the crystal lattice to conduct the electricity in the normal way as happens in the metallic conductors. Hence this is called n-type semiconduction and the material so obtained in known as n-type extrinsic semiconductor. In these materials, the impurity atoms act as charge carriers.

(b) **p-type semiconductors (p-positive hole)**

Here the pure crystal of Si is doped with a minute quantity of gallium, an element of group 13 (Ga: ns^2p^1, i.e. 3 electrons in the valence shell) in which some of the Si atoms are substituted by Ga atoms. Each Ga atom forms three electron pair bonds with neighbouring Si atoms. Fourth neighbouring Si atom forms a weak one electron bond with Ga atom which behaves as free electron at Si atom. This creates electron deficiency or positive hole in the lattice site from where the electron is missing. There are as many positive holes as the number of Ga atoms. At absolute zero, the positive hole is located at Ga atom and free electron at Si atom. At elevated or normal temperature, these free electrons move through the crystal from one vacancy site to another thereby leaving new vacancies or positive holes behind. Thus, it appears that the positive holes are moving though actually it is the flow of electrons that takes place to conduct electric current through the crystal on applying the electric field. The flow of electrons and the movement of positive holes occurs in opposite directions. This process is, therefore, called p-type semi conduction and the material so produced in known as p-type extrinsic semiconductor.

5.6 LATTICE ENERGY OF IONIC CRYSTALS

An ionic crystal lattice consists of a large number of cations and anions which are considered to be hard spheres. These ions arrange themselves in a regular pattern to attain a close packed structure. The system gets stabilized by releasing energy during the packing process, i.e. the potential energy of the system is decreased. This released energy is called the lattice energy of the ionic crystal lattice. Similarly, if the ionic lattice has to be broken down into the constituent ions, the energy required is also known as the lattice energy of the ionic crystal. Thus, the lattice energy of an ionic crystal may be defined in two ways depending on the process of packing of ions or their separation from the crystal-

(a) **"The amount of energy released when one mole of gaseous cations and one mole of gaseous anions are brought closer together to their equilibrium position in the stable lattice, from an infinite distance, to form one mole of ionic crystal".** It is denoted by the letter U.

e.g. $C^+(g) + A^-(g) \longrightarrow C^+A^-(s)$ + Energy released (-U, exothermic process) (s = ionic solid) ……….. (5.1)

(b) **“The amount of energy required to remove the constituent ions of one mole of a solid ionic crystal from their equilibrium position in the crystal to infinite distance”.**

e.g. C^+A^- (s) + Energy released (+ U, endothermic process) $\longrightarrow C^+(g) + A^-(g)$

(s = ionic solid) ……….. (5.2)

In both the processes, the magnitude of the energy is same, i.e., energy released = energy required (absorbed) but the symbol of lattice energy is associated with opposite signs. The lattice energy is a quantitative measure of the stability of any ionic solid.

Factors affecting the magnitude of lattice energy

The lattice energy of ionic crystals depends on the following factors:

(i) Charge on the two ions or the product of charges α lattice energy.Greater the charge on the cation or the anion or greater the product of charges on the ions, greater is the magnitude of lattice energy, U. Thus, the lattice energy of ionic crystals containing polyvalent ions is more than those containing monovalent ions, e.g.

Ionic solids	Na^+F^- <	$Mg^{2+}F_2$ <	$Mg^2\,O^{2-}$
lattice energy (kJ mol^-).	914	2882	3895

and Li^+Cl^- (845 kJ mol^{-1}) < $Ca^{2+}O^{2-}$ (3460 kJ mol^1)

(ii) Interionic distance (r) between the ions or ionic size α $\frac{1}{lattice\ energy}$

Lattice energy is inversely proportional to the interionic distance (r) between the ions. Since r = $r_{C+\ -}$ r_A-, smaller the size of ions, smaller will be the value of r and higher will be value of lattice energy. For example, in case of alkali metal fluorides, the r_{M+} increases from Li^+ to Cs^+ hence energy of these compounds decreases from LiF to CsF:

Ionic solid	Li F >	NaF >	KF >	RbF >	CsF
Lattice energy (kJ mol^-)	1034	914	812	780	744

(iii) Electronic configuration of the cation

Pure ionic crystals are generally formed by the cations having inert gas configuration in their outershell, i.e. ns^2p^6 type. If the cation has non-inert gas/pseudo inert gas configuration in the outer shell, i.e. $ns^2p^6\ d^{10}$ type, this involves covalent character in the ionic bond of the crystal thereby increasing the lattice energy of the crystal. For example, AgCl(904kJ mol^{-1}) has larger value of lattice energy than that of NaCl (788kJ mol^{-1}). AgCl has significant covalent character while NaCl is essentially ionic because Ag^+ has $ns^2p^6d^{10}$ outer shell configuration and Na^+ has ns^2p^6 type configuration.

Effect of lattice energy on crystals

(i) **Solubility**- For an ionic solid to be dissolved in a solvent, the strong forces of attraction between its ions (i.e. lattice energy) must over come by the ion-solvent interaction energy called solvation energy (which is released during this interaction). For non-polar solvents, solvation energy is small so ionic solids do not dissolve in them because lattice energy > solvation energy. In a polar solvent like water, generally, ionic solids dissolve because the solvation energy> lattice energy and thus ion-solvent interaction breaks the ionic solid into constituent ions which are solvated and go into the solution.

There are some ionic solids which do not dissolve in polar solvents, *viz*. water. For example, AgCl in insoluble in water. This is due to greater cohesive forces in AgCl resulting from covalent character of ionic bond. $BaSO_4$, $SrSO_4$, $PbSO_4$ etc. are also insoluble in water due to very high lattice energy of these crystals.

(ii) **Melting point** - As the lattice energy increases, the melting point also increases.

5.7 BORN-HABER CYCLE: EXPERIMENTAL DETERMINATION OF LATTICE ENERGY OF AN IONIC SOLID

Since direct experimental determination of lattice energies are not easy, there are determined by indirect method using a thermo-chemical cyclic process known as Born-Haber cycle. To illustrate this, we take example of formation of compound MX(s) from M(s) and X_2(g). The different steps involved in the formation of MX(s) in crystalline state are as given below;

(i) Sublimation of M (s) to M (g). In this step 1 mole of solid M absorbs energy equal to its sublimation energy, $(\Delta H_{sub})_M$ and is converted to gaseous state, M(g), this is an endothermic process. (Energy is absorbed)

$$\underset{(1\text{mole})}{M(s)} + (\Delta H_{sub})_M \longrightarrow \underset{(1\text{mole})}{M(g)} \quad \ldots..(5.3)$$

(ii) Dissociation of $\frac{1}{2}X_2$ (g) to X (g). In this step half mole of X_2 (g) absorbs energy equal to half of the dissociation energy X_2 (g), $\frac{1}{2}(\Delta H_{diss.})_{X_2}$ and is converted to X (g). It is an endothermic process. (Energy is absorbed):

$$\underset{(1\text{mole})}{\frac{1}{2}X_2(g)} + \frac{1}{2}(\Delta H_{diss.})_{X_2} \longrightarrow X(g) \quad \ldots\ldots\ldots\ldots(5.4)$$

(iii) Ionisation of M (g) to M^+ (g). Each M (g) atom absorbs energy equal to its ionisation energy $(IE)_M$ and loses its outermost electron to form M^+(g). It is an endothermic process. (Energy is absorbed):

$$\underset{(1mole)}{M\,(g)} + (IE)_M \longrightarrow \underset{(1mole)}{M^+\,(g)} + e^- \qquad \text{…………..(5.5)}$$

(iv) Conversion of X(g) into X^- (g). The X (g) atom gains electron given by M(g) above to its outer shell to form X^- (g). In this process X(g) releases energy equal to its electron affinity or affinity energy $(EA)_X$. This is an exothermic process (Energy is released):

$$\underset{(1mole)}{X\,(g)} + e^- \longrightarrow \underset{(1mole)}{X^-\,(g)} - (EA)_X \qquad \text{…………(5.6)}$$

(v) Combination of M^+ (g) and X^- (g) to form MX (solid). This is the final step in which M^+ (g) and X^- (g) formed as above combine together to form MX(s). In this process energy equal to lattice energy of MX, $(U)_{MX}$ is released. This is also an exothermic process and energy is released:

$$\underset{(1mole)}{M^+\,(g)} + \underset{(1mole)}{X^-\,(g)} \longrightarrow \underset{(1mole)}{MX\,(s)} - (U)_{MX} \qquad \text{…………(5.7)}$$

The overall change as illustrated above may be represented in one direct step, as;

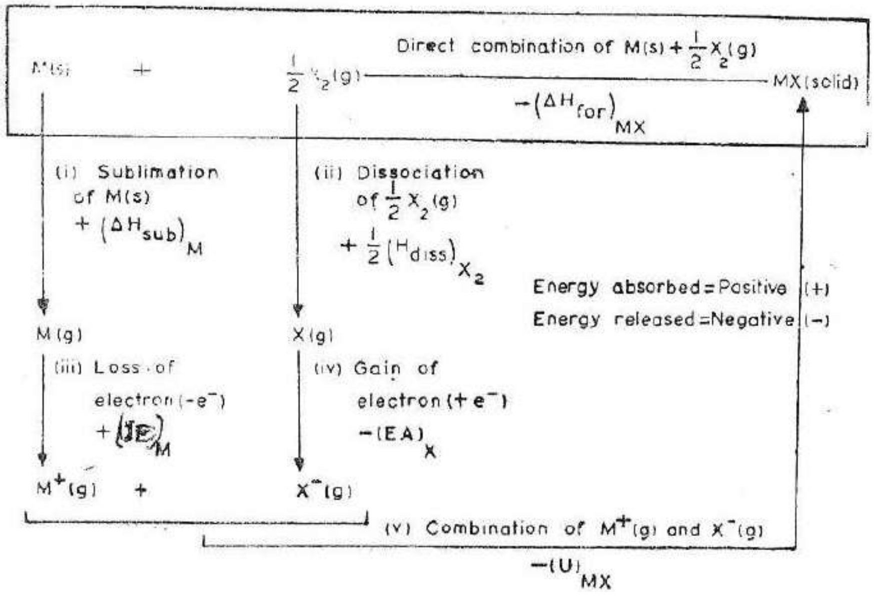
$$M\,(s) + \tfrac{1}{2}\,X_2\,(g) \longrightarrow MX\,(crystal) - (\Delta H_{for})_{MX}\ \text{(exothermic process) …..(5.8)}$$

According to Hess's Law, the heat of formation (total enthalpy change) of MX, $(\Delta H_{for})_{MX}$ must be same irrespective of the fact weather it takes place directly in one step or through a number of steps as illustrated above. Hence,

$$-(\Delta\,H_{for})_{MX} = (\Delta\,H_{sub})_M + \tfrac{1}{2}(\Delta\,H_{diss})x_2 + (I_E)_M - (E_A)_X - (U)_{MX} \qquad \text{……….(5.9)}$$

Here energy terms of endothermic processes are associated with positive sign and those of exothermic processes with negative sign. With the help of the above final equation we can determine the value of $(U)_{MX}$ if the quantitative values of other energy terms are known and placing these values in the equation along with their algebraic signs. NaCl may be taken as an example.

The whole act of above processes can also be given diagrammatically as shown below:



Applications of Born-Haber Cycle:

(i) Born-Haber cycle can be used to obtain any one of the six energy values for the six appropriate equations given above. In particular, the value of electron affinity of the non-metals which is most difficult to determine experimentally can be obtained by this method.

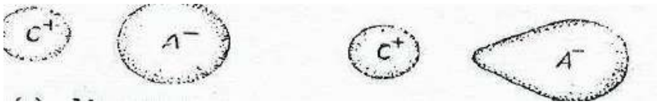
(ii) This cycle is useful in establishing the stability of ionic compounds. It is generally observed that the lattice energy for a compound is known but standard enthalpy of formation is not. So standard enthalpy of formation can be obtained with the help of Born-Haber cycle.

(iii) This cycle helps to understand the disproportionation reactions from lower to higher oxidation states in metal salts, i.e. most metals fail to form stable ionic compounds in low oxidation states such as MnCl, CaCl, AlO etc, If Born – Haber cycle is compared for MCl and MCl_2 (M = Mg, Ca etc). it can be shown that the formation of MCl_2 in favoured over that of MCl. The much higher lattice energy of MCl_2 over that of MCl is the answer to this question.

5.8 FAJAN’S RULES; POLARISATION OF IONS

In an ionic solid, both cation and anion are maintained at an equilibrium distance but when a cation approaches an anion closely, the net positive charge on the cation attracts the electron cloud of anion and at the same time the cation also repels the positive nucleus of anion. The combined effect of these two forces, attractive and repulsive, is that the electron cloud of anion (being larger in size) no longer remains symmetrical but is shifted towards the cation.

This is called distortion or polarization of the anion by the cation and anion is said to be polarised. The ability of cation to polarise a nearby anion is called its polarising power.



Unpolarised anion

Polarised anion

Fig. 5.6 Polarisation of anion

The anion also polarises a cation but due to the larger size of anion, it polarises a cation to a lesser extent (or almost negligible) while the polarisation of anion by a cation is appreciable, i, e. the anions are more susceptible to get polarised. Thus, in general, the cations have high polarising power and anions have more polarisability, i.e. the tendency to get polarised.

Due to the polarisation of anion by the cation, the electron cloud of anion is concentrated between the nuclei of two ions and behaves as if it is being shared by the two ions. Because of this tendency, the ionic bond in the compound passes to the covalent bond, i.e. has covalent character. There are certain factors which affect the polarisation of the ions, These are known as Fajan's rules.

Fajan's Rules: These rules are as follows:

(i) **Charge on the cation or the anion**

Generally the polarising power of a cation increases with increasing positive charge on it. This is because a cation having higher charge can attract electrons effectively. This can be seen in the anhydrous chlorides, *viz.* NaCl, $MgCl_2$ and $AlCl_3$. With increasing polarising power of cation, the covalent character of the bond between the cation and the anion also increases. Because the covalent compounds have lower melting points, therefore in the above chlorides the polarising power increases in the order: $Na^+ < Mg^{2+} < Al^{3+}$ and accordingly the melting points decrease from NaCl to $AlCl_3$ as given below:

Compound : Nacl $< MgCl_2 < AlCl_3$ (covalent character increases)

Melting point (^{0}C) : 800 > 712 > 575

Similarly, the polarisability of an anion increases with increasing negative charge on it because the outer electron cloud is loosely held by the nucleus of the anion and also the anion can repel its outer electrons more effectively. Thus the oxide ions, O^{2-} in the oxides of metals are more polarised than (say) F^-ions in the fluorides of the same metals and hence the oxides are more covalent than fluorides having lower melting points.

(ii) **Size of the cation (cationic radii)**

Smaller the cationic size, closer it can go to the anion and more is its polarising power. Thus, with increasing cationic size, the power of cation to polarise an anion decreases which decreases the covalent character of the bond between the ions. This increases the melting points of the compounds. Let us take anhydrous chlorides of group 2nd elements, *viz*. Becl$_2$, $MgCl_2$, $CaCl_2$, $SrCl_2$, $BaCl_2$ and $RaCl_2$. The cationic size and melting points of these chlorides are given below:

Metal chloride	$BeCl_2$	$MgCl_2$	$CaCl_2$	$SrCl_2$	$BaCl_2$	$RaCl_2$
Cation present	Be^{2+}	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}	Ra^{2+}
Cationic size (Å)	0.31	< 0.65	< 0.99	<1.13	< 1.35	< 1.40
Melting point (^{0}C)	405	< 712	< 772	<872	< 960	< 1000

The covalent character decreases with increasing cationic size and melting point of the compound and hence ionic character increases.

(iii)**Size of the anion (anionic radii)**

Larger the anionic size, more is its polarisalility, i.e. the tendency to get polarsed. With increasing anionic size, the polarisalility also increases thereby increasing the covalent character in the bond and consequently decreasing the melting point of the compounds. Calcium halides may be taken as examples.

Calcium halide	CaF_2	$CaCl_2$	$CaBr_2$	CaI_2	The covalent character of
Anion present	F^-	Cl^-	Br^-	I^-	the halides increases.
Anionic size (Å)	1.36	<1.81	< 1.95	<2.16	
Melting point (^{0}C)	1392	> 772	> 730	> 575	

(iv) **Electronic configuration of the cation**

A Cation with pseudo inert gas electronic configuration (i.e. $ns^2p^6d^{10}$) in its outer most shell (18 electrons) has greater polarising power, due to greater Zeff, to polorise an anion than a cation with inert gas configuration (i.e. ns^2p^6) in its outer shell (8 electrons) even if both type of cations have the same size and charge. Thus the first type of cation will polarise the anion to a greater extent thereby resulting in a more covalent bond with lower melting point of the compound. Let us look at two chlorides, *viz.* AgCl and KCl, Ag^+ ion has $4s^2p^6d^{10}$ outer shell electronic configuration and gives more covalent AgCl (m.p. 455^0C) than KCl (m.p. 776^0C) which has K^+ ion with $3s^2p^6$ outer shell configuration.

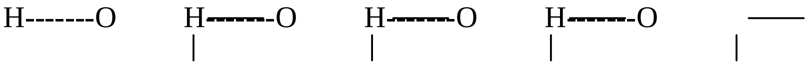
5.9 WEAK INTERACTIONS

The force that holds the atoms together in a molecule is called a chemical bond. These bonds *viz.* ionic bond, covalent bond and coordinate covalent bond are formed due to strong attraction tendency between the species. The resulting products, i.e. the molecules or their aggregates (sometimes) are stable species. But there are instances where only weak bonds exist between/amongst different species, for example within molecules. In these cases, we say that molecular forces are present between the molecules. Such species are said to have formed by weak interactions. Hydrogen bonding and van der waals' forces are common examples of such molecular forces causing weak interactions.

5.9.1 Hydrogen Bonding:

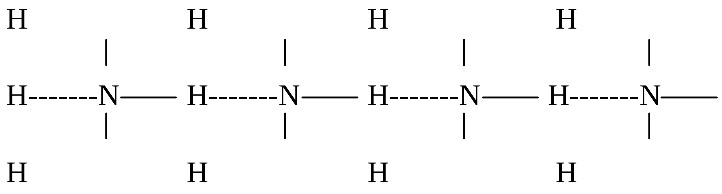
This is a peculiar type of bonding which has been named after an element, hydrogen and operates between the molecules containing hydrogen and an atom of the electronegative elements. It is defined as "**the electrostatic force of attraction between H-atom linked covalently to an atom of highly electronegative element like F, O, N etc. in a molecule and another atom of a highly electronegative elements of the same or different molecule**". Thus hydrogen bond may be formed either between the molecules of same substance or between the molecules of different substances. It is a weak bond formed by the weak interaction and is represented by dotted line (……).

The common examples in which hydrogen bonding exists are:



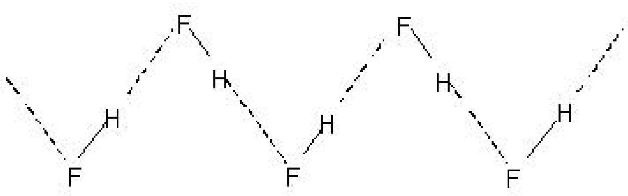
H H H H

$(H_2O)_x$ Cluster

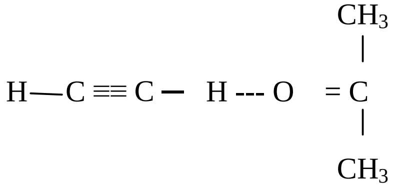


$$\begin{matrix} \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & \\ & | & & | & & | & & | \\ \mathrm{H}\text{-------} & \mathrm{N}\text{——} & \mathrm{H}\text{-------} & \mathrm{N}\text{——} & \mathrm{H}\text{-------} & \mathrm{N}\text{——} & \mathrm{H}\text{-------} & \mathrm{N}\text{——} \\ & | & & | & & | & & | \\ \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & \end{matrix}$$

$(NH_3)_x$ cluster



$(HF)_x$ cluster



$$\mathrm{H{-}C{\equiv}C{-}\ \ H\text{ --- }O\ = \underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}}$$

Hydrogen bonding taking place between the molecules of same substance or different substances.

Cause of hydrogen bond formation

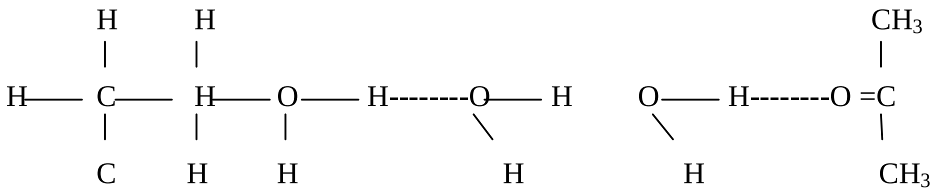
When H-atom is linked with an atom of highly electronegative element (say) A atom (Amay be F, O, N etc.) to form a polar covalent molecule HA, the molecule develops polarity like $H^{\delta+}$-$A^{\delta-}$ due to electronegativity difference between H and A-atoms. If this molecule comes closer to another such molecule, e.g. $H^{\delta+}$-$A^{\delta-}$ or $H^{\delta+}$-$B^{\delta-}$ (B may also be F, O, N etc.), the two dipoles will be linked together by a special type of bond through hydrogen atom, called hydrogen bond: A^{δ} -$H^{\delta+}$----- B^{δ} -$H^{\delta+}$ Here H-atom acts as a bridge between electronegative atoms A and B. This process may be repeated for several molecules to give a cluster of molecules where H– bond is formed between any two adjacent molecules of the aggregate or cluster.

Types of Hydrogen bonding

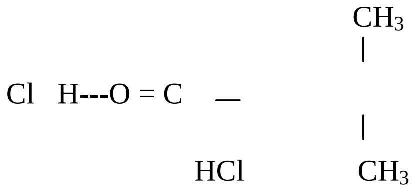
The hydrogen bonding in the compounds has been found of two types:

(i) **Intermolecular hydrogen bonding (molecular association)**

This type of H-bonding takes place between several molecules of the same substance or different substances. The molecules get associated as a result of H-bonding to give a large cluster. This process is known as association. The examples of this type of H-bonding are H_2O, NH_3, HF etc. which have been shown above in the beginning of this topic where association of similar type of molecules occurs. Association of C_2H_2 (acetylene)and CH_3COCH_3(acetone) has also been shown above. Other examples of intermolecular H-bonding are given below between the molecules of different substances:



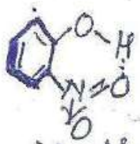
Alcohol water Acetone



Acetone

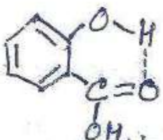
(ii) **Intramolecular hydrogen bonding (**Chelating)

This type of hydrogen bond is formed between the two atoms of the same molecule, one of the atoms being H-atom. It may lead to the linking of two groups of a molecule to form a ring structure, the ring being generally, a five-membered or a six–membered chelate ring (meaning claw). The examples in which intramolecular hydrogen bonding occurs are aromatic organic molecules *viz.* o-nitrophenol, o-chlorophenol, salicylic acid, salicylaldehyde etc.



O-nitrophenol

O-chlorophenol



salisilic acid,

Strength of H-bond

As has been stated above that this bond is a weak bond since it is merely an electrostatic force of attraction and not a chemical bond. The strength of H-bond increases with increasing electronegativity of the atom attached with H-atom by a covalent bond, i.e. N, O, and F. This bond is much stronger than van der Waals' force but about ten times weaker than a covalent bond. The order of the strength may be given as: van der Waals' forces < H-bond < covalent bond < ionicbond.

Consequences of hydreogen bonding

Hydrogen bonding largely affects a number of physical properties of H-bonded compounds. Some of them are given below:

(i) Melting and boiling points of hydrides of group 15,16 and 17 elements; the hydrides of N, O and F among those of other elements of these groups show abnormal melting and boiling points. This is attribute to the association of molecules caused by the formation of hydrogen bonds. Let us take hydrides of group 16 elements, *viz*. H_2O, H_2S, H2Se & H_2Te. The melting and boiling points of H_2O are exceptionally high in comparison to those of other hydrides which show the increasing trends in these properties, i.e. $H_2O >> H_2S > H_2Se > H_2Te$ (both m.p. and b.p.)

(ii) Density of ice and water; like every solid crystal, ice has definite lattice structure in which water molecules are arranged in such a way that every water molecule is surrounded by four other water molecules in tetrahedral fashion. The central H_2O molecule is linked to four other H_2O molecules by hydrogen bonding (See Fig. 5.7). Because H-bonds are weaker and longer than covalent bonds, this arrangement gives a three dimensional open cage like structure with large empty space within the structure. This increases the volume and decreases the density of ice. That is way ice floats on water surface.

In liquid form water molecules lie closer together hence the same mass of water has smaller volume and its density is more than that of ice.

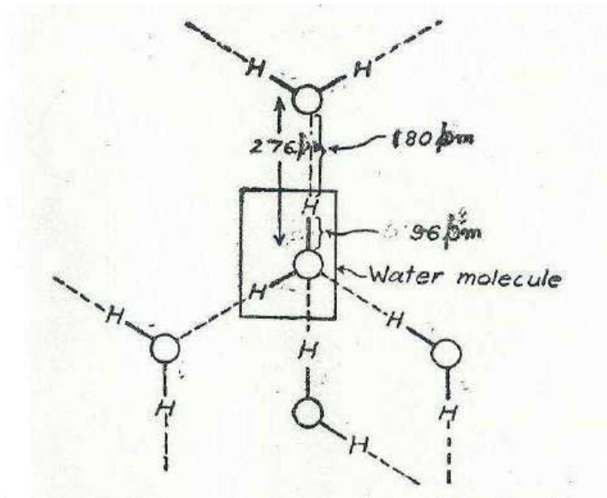


Fig. 5.7 Open cage like crystal structure of ice

(iii) Density of water is maximum a 4^0C; When ice melts, the cage like structure breaks down and the molecules of water are packed closely together, thereby decreasing the volume. The breaking of structure (i.e. hydrogen bonds) is not completed until the temperature reaches 4^0C. Above 4^0C, expansion commences thereby increasing the volume. Thus, the volume of water is minimum and density is maximum (density = $\frac{mass}{volume}$) at 4^0c.

5.9.2 van der Waals' Forces (or Intermolecular forces):

The weak attractive forces between the uncharged atoms or molecules of polar as well as non-polar substances are collectively referred to as van der Waals' forces. The magnitude of these forces is maximum for solids and decreases for liquids and minimum for gases. The crystals whose constituent particles are held together in position by these forces are called molecular crystals. These forces arise from the electrostatic attraction of the nuclei of one molecule for the electrons of a different molecule. The repulsions between the electrons of the two molecules and the nuclei of the two molecules try to counter balance the electrostatic attractions but there is always a small net attractive force. Van der Waals' forces are short range forces. These forces are due to different type of interactions which are given below:

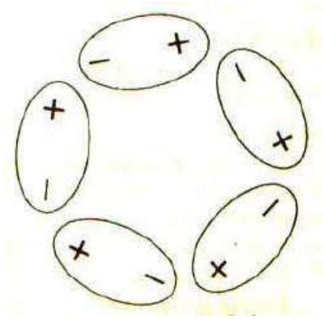


Fig. 5.8 Dipole-dipole interaction (head to tail arrangement)

(i) **Dipole-dipole interaction**

These interactions are present in polar molecules like NH_3, SO_2, HCl etc. (all gases). Although these molecules are neutral, they have permanent dipole moments and behave as dipoles. Larger the dipole moment of a molecule, greater is the dipole-dipole attractive force between the molecules. Actually in the dipoles, the van der Waals' forces are due to the electrostatic interactions between the positive end of one dipole and the negative end of the other dipole.

(ii) **Ion-dipole interaction**

If a charged particle such as an ion is introduced into the neighbourhood of an uncharged nonpolar molecule (e.g. an atom of a noble gas), it will distort the electron cloud of the atom or molecule in the same way as a cation does on a large anion (polarisation). The polarisation of neutral species depends on its inherent polarisability and polarising field afforded by the charged ion (±). Such interactions occur only in solution of ionic compounds in non-polar solvents.

(iii) **Dipole- induced dipole interaction**

A dipole can induce an uncharged non-polar species into a dipole as does an ion in ion dipole interaction. Then there occurs dipole induced dipole interaction. These are important only in solution of polar compounds in non-polar solvents.

(iv) **London or dispersion forces** (instantaneous dipole-induced dipole interactions)

These interactions are present in non-polar molecules like N_2, O_2, Cl_2, CH_4 etc. and mono atomic molecules like He, Ne, Ar etc. These molecules do not have permanent dipole moment. The average electronic distribution in a non-polar molecule is symmetric but because of continuous motion of the electrons, at any given instant, the centres of negative and positive charges may not coincide. This causes a momentary distortion of the electronic charge cloud which results in an instantaneous temporary polarity. Then this instantaneous dipole may induce polarity in another non-polar atom/molecule. These two dipoles attract each other by electrostatic forces called London forces.

Since van der Waals' forces are weak and may be easily overcome, the condensed gas readily vapourises and molecular crystals are soft and have low melting points.

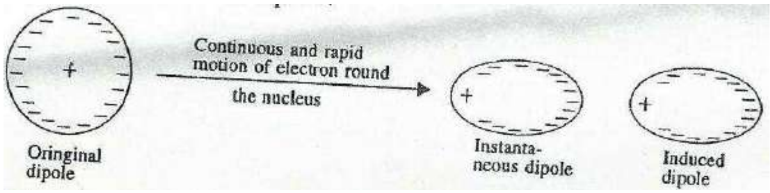


Fig. 5.9 Instantarery dipole dipole induced dipole interaction between non-polar

5.10 SUMMARY

This unit consists of a brief discussion of ionic solids, their characteristics, the interesting topic of radius ratio and its effect, crystal coordination number and limitations of radius ratio rule. The lattice defects have been fruitfully discussed and an elaborate account of semiconductors has been given. A concise account of lattice energy, the factors affecting its magnitude and its experimental determination has been discussed. The rules governing the covalent character of ionic bond, a brief discussion of H-bond and van der Waals' forces have also been taken care offor the readers.

5.11 TERMINAL QUESTIONS

i. The coordiniation number of Cl^- ion in NaCl crystal is:

(a) 4 (b) 6 (c) 8 (d) 12

ii. CsCl crystal has the packing pattern of ions:

(a) Cubic (b) Tetrahedral (c) Octahedral (d) Square planar

iii. If one cation and one anion are missing from their positions in a crystal lattice, the defect produced is:

(a) Schottky defect (b) Frenkal defect (c) n-type defect (d) p-type defect

iv. Which one of the following will have covalent character?

(a) LiCl (b) NaCl (c) KCl (d) CsCl

v. How do the ionic crystals behave towards the electric field applied on them in solid state, fused state and in solution?

vi. Give a brief account of n-type semi conductors.

vii. How is lattice energy of an ionic compound related with its solubility in polar solvent?

viii. What is polarization of ions?

ix. What is the cause of H-bonding in the compounds?

x. We have two cations. One of them has pseudo inert gas outer shell electronic configuration and the other has inert gas configuration in the outer shell. Which of these will cause more polarisation of an anion?

xi. Give a brief account of London forces.

5.12 ANSWERS

i. (b)
ii. (a)
iii. (a)
iv. (a)
v. Please refer to characteristics of ionic compounds.
vi. Please see semiconductors.
vii. Please refer to the effect of lattice energy on crystals.
viii. Please refer to polarisation and Fajan's rules.
ix. Please see H-bonding.
x. Please refer to Fajan's rules.
xi. Please see van der Waals' forces.

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