CHEMICAL BONDING

1. INTRODUCTION

Atoms are usually not capable of free existence but groups of atoms of the same or different elements exist as one species, e.g., H_2, O_2, P_4, S_8, H_2O.

A group of atoms existing together as one species and having characteristic properties is called a molecule.

Obviously, there must be some force which holds these atoms together within the molecules.

2. CHEMICAL BOND

This force which holds the atoms together within a molecule is caled a chemical bond.

2.1 Why do atoms combine ?

Lewis-Kossel Approach to Chemical Bonding

The atoms of different elements combine with each other in order to complete their respective octets (i.e., 8 electrons in their outermost shell) or duplet (i.e., outermost shell having 2 electrons) in case of H, Li and Be to attain stable nearest noble gas configuration.

2.2 Modes of Chemical Composition
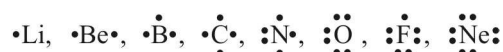
This can occur in two ways :

1. By complete transference of one or more electrons from one atom to another. This process is referred to as electrovalency and the chemical bond formed is termed as electrovalent bond or ionic bond.

2. By sharing of electrons. This can occur in two ways as follows :

   (a) When the shared electrons are contributed by the two combining atoms equally, the bond formed is called covalent bond.

   (b) When these electrons are contributed entirely by one of the atoms but shared by both, the bond formed is known as a coordinate bond, also called dative bond.

3. LEWIS SYMBOLS

In the formation of a molecule, only the outer shell electrons are involved and they are known as valence electrons. The inner shell electrons are well protected and are generally not involved in the combination process. It is, therefore, quite reasonable to consider the outer shell electrons, i.e., valence shell electrons while discussing chemical bonds.

G.N. Lewis introduced simple symbols to denote the valence shell electrons in an atom. The outer shell electrons are shown as dots surrounding the symbol of the atom. These symbols are known as Lewis symbols or electron dot symbols. These symbols ignore the inner shell electrons. A few examples are given below :

$\bullet$Li, $\bullet$Be$\bullet$, $\bullet\overset{\bullet}{B}\bullet$, $\bullet\overset{\bullet}{C}\bullet$, $:\overset{\bullet}{N}\bullet$, $:\overset{\bullet\bullet}{\underset{\bullet\bullet}{O}}$, $:\overset{\bullet\bullet}{\underset{\bullet\bullet}{F}}:$, $:\overset{\bullet\bullet}{\underset{\bullet\bullet}{Ne}}:$
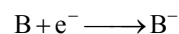
4. IONIC BOND

When a bond is formed by complete transference of electrons from one atom to another so as to complete their outermost orbits by acquiring 8 electrons (i.e., octet) or 2 electrons (i.e., duplet) in case of hydrogen, lithium etc. and hence acquire the stable nearest noble gas configuration, the bond formed is called ionic bond or electrovalent bond.

4.1 Explanation of Ionic Bond

Atoms are electrically neutral. Therefore, they possess equal number of protons and electrons. On losing an electron, an atom becomes positively charged since now the number of protons exceeds the number of electrons.
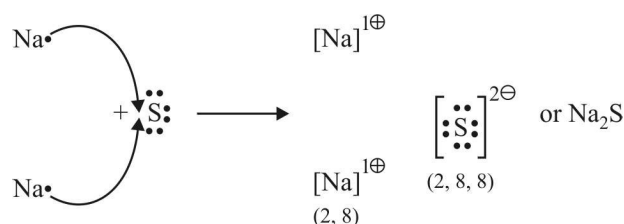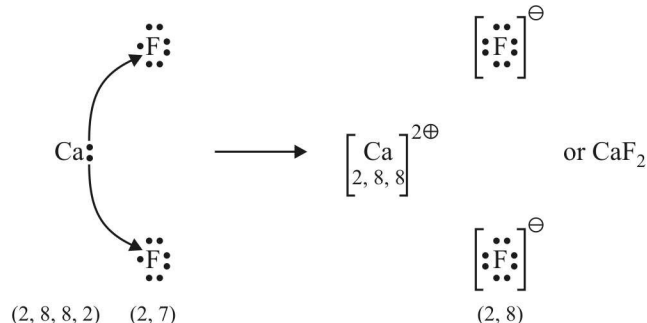
$$A \longrightarrow A^+ + e^-$$
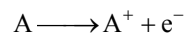
On the other hand, in case of atom, gaining the electron, the number of electrons exceeds the number of protons and thus the atom becomes negatively charged.

$$B + e^- \longrightarrow B^-$$

The oppositely charged particles formed above attract each other by electrostatic forces of attraction. The bond thus formed is known as electrovalent or ionic bond.

Examples

4.2 Electrovalency

The number of electrons lost or gained during the formation of an electrovalent linkage is termed as the electrovalency of the element.

For example, sodium and calcium lost 1 and 2 electrons respectively and so their valencies are 1 and 2. Similarly, chlorine and oxygen gain 1 and 2 electrons respectively, so they possess an electrovalency of 1 and 2. In other words, valency is equal to the charge on the ion.

4.3 Factors governing the formation of ionic bonds

(i)   Ionisation Enthalpy (Ionization Energy)

Ionisation enthaly of any element is the amount of energy required to remove an electron from the outermost shell of an isolated atom in gaseous phase so as to convert it into a gaseous positive ion.

It is clear that lesser the ionisation enthalpy, easier will be the removal of an electron, i.e., formation of a positive ion and hence greater the chances of formation of an ionic bond. Ionisation enthalpy (I.E.) of alkali metals (i.e., group I elements) is low, hence they have more tendency to form positive ions.

(ii)   Electron Gain Enthalpy (Electron Affinity)

Electron affinity or Electron gain enthalpy of an element is the enthalpy change that takes place when an extra electron is added to an isolated atom in the gaseous phase to form a gaseous negative ion.

Higher is the electron affinity, more is the energy released and stabler will be the negative ion produced. Consequently, the probability of formation of ionic bond will be enhanced. Halogens possess high electron affinity. So the formation of their negative ions is very common, e.g., in case of chlorine, electron affinity is +348 kJ/mole, i.e.,

$Cl(g) + e^- \rightarrow Cl^- + 348$ kJ/mole
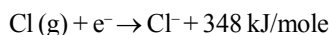
or   E.Z. $= +348$ kJ mol^{-1}

(iii)   Lattice Enthalpy (Lattice Energy)

In the formation of ionic compounds, the positively charged ions combine with negatively charged ions to form the compound.

$A^+(g) + B^-(g) \rightarrow A^+B^-(s)$
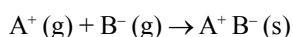
The energy released when the requisite number of gaseous positive and negative ions combine to form one mole of the ionic compound is called lattice enthaly.

4.4 Characteristics of Ionic Compounds

1.   Physical State

These compounds usually exist in the solid state.

2.   Crystal Structure

X-ray analysis of the ionic compounds shows that they exist as ions and not as molecules. These ions are arranged in a regular pattern in the three dimensional space to form a lattice.

The pattern of arrangement, however, depends upon the size and charges of the ions. For example, in case of sodium chloride, each sodium ion is surrounded by six chloride ions and each chloride by six sodium ions, thus giving rise to a three dimensional octahedral crystal structure (figure). The formula of an ionic compound merely indicates the relative number of ions present.
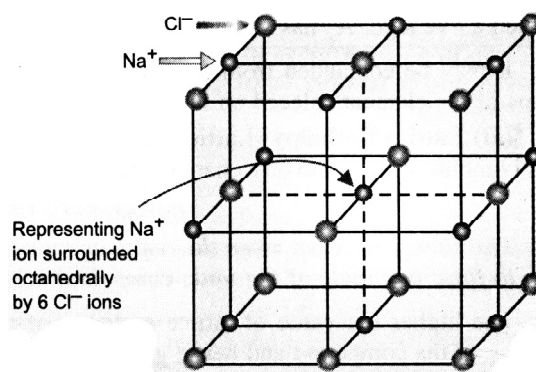
Crystal structure of NaCl

3.   High melting and boiling points

Ionic compounds possess high melting and boiling points. This is because ions are tightly held together by strong electrostatic forces of attraction and hence a huge amount of energy is required to break the crystal lattice.

4.   Solubility

Electrovalent compounds are soluble in solvents like water which are polar in nature and have high dielectric constant. It is due to the reason that the polar solvent interacts with the ions of the crystals and further the high dielectric constant of the solvent (i.e., capacity of the solvent to weaken the forces of attraction) cuts off the force of attraction between these ions. Furthermore, the ions may combine with the solvent to liberate energy called the hydration enthalpy which is sufficient to overcome the attractive forces between the ions.

Non-polar solvents like carbon tetrachloride, benzene etc. having low dielectric constants are not capable of dissolving ionic solids. Hence, ionic solids are soluble in polar solvents and insoluble in non-polar solvents.

5.   Electrical conductivity

Ionic compounds are good conductors of electricity in solution or in the molten state. In solution or molten state, their ions are free to move. As the ions are charged, they are attracted towards electrodes and thus act as carriers of electric current.
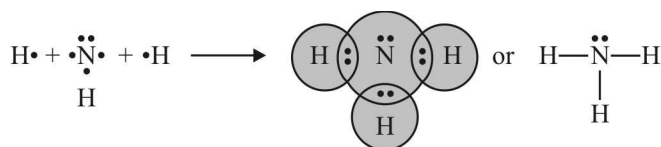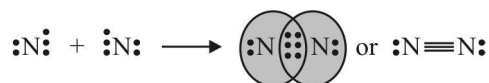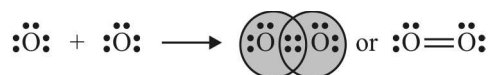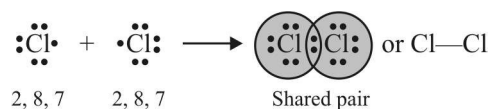
6. Ionic Reactions

The reactions of the ionic compounds are, in fact, the reactions between the ions produced in solution. As the oppositely charged ions combine quickly, these reactions are, therefore, quite fast.

[e.g. $Na^+Cl^-(aq) + Ag^+NO_3^-(aq) \rightarrow AgCl(s) + NaNO_3(aq)$]
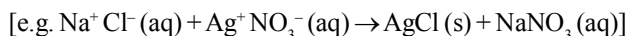
5. COVALENT BOND

The bond formed between the two atoms by mutual sharing of electrons between them so as to complete their octets or duplets in case of elements having only one shell is called covalent bond or covalent linkage and the number of electrons contributed by each atom is known as covalency.

Example

:Cl• + •Cl: ⟶ (:Cl:Cl:) or Cl—Cl
2, 8, 7   2, 8, 7   Shared pair

:O: + :O: ⟶ (:O::O:) or :O=O:

:N: + :N: ⟶ (:N:::N:) or :N≡N:

H• + •N• + •H ⟶ (H(:)N(:)H) or H—N—H
     | | |
     H   H   H

Example

Draw the Lewis dot structure of HCN molecule.

Sol. Step-1 : Total number of valence electrons in HCN = 1 + 4 + 5 = 10 ($_1$H = 1, $_6$C = 2 ,4 ,$_7$N = 2, 5)

Step-2 : Skeletal structure is HCN (C is least electronegative).

Step-3 : Putting one shared pair of electrons between H and C and one between C and N, and the remaining as lone pairs, we have

H:C:N:

In this structure, duplet of H is complete but octets of C and N are not complete. Hence, multiple bonding is required between and N. Octets of C and N will be complete if there is triple bond between C and N. Thus,
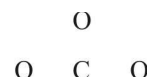
H:C:::N or H—C≡N
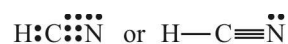
Example

Draw the Lewis dot structure of CO_3^{2-} ion.

Sol. Step-1 : Total number of valence electrons of CO_3

= 4 + 3 × 6 = 22 ($_6$C = 2, 4, $_8$O = 2, 6)

Step-2 : Total number of electrons to be distributed in CO_3^{2-}

= 22 + 2 (for two units -ve charge) = 24

Step-3 : The skeletal structure of CO_3 is

O

O   C   O

Step-4 : Putting one shared pair of electrons between each C and O and completing the octets of oxygen, we have

:O:
:O:C:O:

In this structure, octet of C is not complete. Hence, multiple bonding is required between C and one of the O–atoms. Drawing a double bond between C and one O-atom serves the purpose :
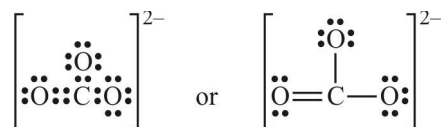
$$\left[\begin{array}{c} :O: \\ :O::C:O: \end{array}\right]^{2-} \quad \text{or} \quad \left[\begin{array}{c} :O: \\ | \\ :O=C—O: \end{array}\right]^{2-}$$

Table : Lewis structures of some typical molecules and ions

	Molecule/ Ion	Lewis Representation		
(i)	CO	:C::O:	or	:C≡O:
(ii)	CO_2	Ö::C::Ö	or	Ö=C=Ö
(iii)	O_2	:Ö::Ö:	or	:Ö=Ö:
(iv)	O_3	(Lewis dot structure)	or	(Lewis structure with double bond)
(v)	H_2O_2	H:Ö:Ö:H	or	H—Ö—Ö—H
(vi)	SO_3	:Ö::S:Ö: / :Ö:	or	:Ö=S—Ö: / :Ö:
(vii)	$HClO_4$ (Perchloric acid)	:Ö: / H:Ö:Cl:Ö: / :Ö:	or	:Ö: / H—Ö—Cl—Ö: / :Ö:
(viii)	HNO_2 (Nitrous acid)	H:Ö:N::Ö:	or	H—Ö—N=Ö:
(ix)	HNO_3 (Nitric acid)	:Ö: / H:Ö:N / :Ö:	or	H—Ö—N(=Ö:)(:Ö:)
(x)	H_3PO_4 (Phosphoric acid)	:Ö:H / H:Ö:P:Ö:H / :Ö:	or	:Ö—H / H—Ö—P—Ö—H / :Ö:
(xi)	CN^- (Cyanide ion)	[:C::N:]⁻	or	[:C≡N:]⁻
(xii)	NO_2^- (Nitrite ion)	[Ö::N:Ö:]⁻	or	[Ö=N—Ö:]⁻
(xiii)	NO_3^- (Nitrate ion)	[Ö::N:Ö: / :Ö:]⁻	or	[Ö=N—Ö: / :Ö:]⁻
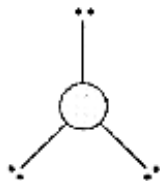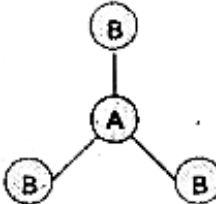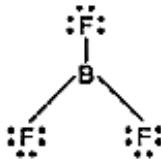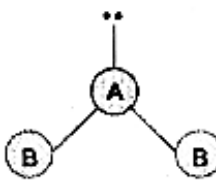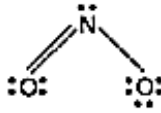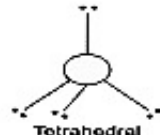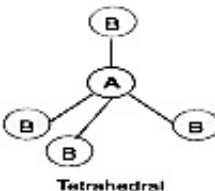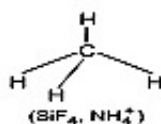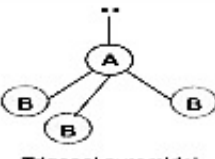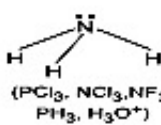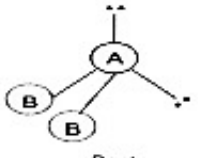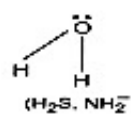
Table : Lewis structures of some typical molecules and ions
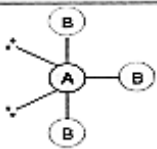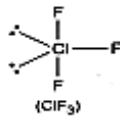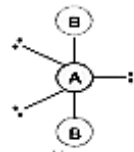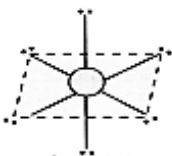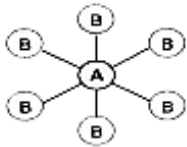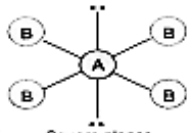
	Molecule/ Ion	Lewis Representation		
(xiv)	SO_4^{2-} (Sulphate ion)	[:Ö: / :Ö:S:Ö: / :Ö:]²⁻	or	[:Ö: / :Ö—S—Ö: / :Ö:]²⁻
(xv)	O_2^{2-} (Peroxide ion)	[:Ö:Ö:]²⁻	or	[:Ö—Ö:]²⁻
(xvi)	H_3O^+ (Hydronium ion)	[H:Ö:H / H]⁺	or	[H—Ö—H / H]⁺

6. FORMAL CHARGE

The formal charge on an atom in a molecule or ion is defined as the difference between the number of valence electrons of that atom in the free state and the number of electrons assigned to that atom in the Lewis structure, assuming that in each shared pair of electrons, the atom has one electron of its own and the lone pair on it belongs to it completely. Thus, it can be calculated as follows :

$$\begin{bmatrix} \text{Formal charge (F.C.) on} \\ \text{an atom in a molecule / ion} \end{bmatrix} = \begin{bmatrix} \text{Total no. of valence electrons} \\ \text{in the free atom} \end{bmatrix} -$$

$$\begin{bmatrix} \text{Total no. of electrons of} \\ \text{lone pairs (non – bonding electrons)} \end{bmatrix} - \frac{1}{2}$$

$$\begin{bmatrix} \text{Total no. of shared electrons} \\ \text{(bonding electrons)} \end{bmatrix}$$

i.e., $FC = V - L - \frac{1}{2}S$

Example

Calculate formal charge on each O-atom of O_3 molecule.

Sol. Lewis structure of O_3 is :

The atoms have been numbered as 1, 2 and 3.
Formal charge on end O-atom numbered 1

$$= 6 - 4 - \frac{1}{2}(4) = 0$$

Formal charge on central O-atom numbered 2

$$= 6 - -\frac{1}{2}(6) = +1$$

Formal charge on end O-atom numbered 3

$$= 6 - 6 - \frac{1}{2}(2) = -1$$

Hence, we represent O_3 along with formal charges as :

Example

Write the formal charges on atoms in (i) carbonate ion (ii) nitrite ion.

Sol. (i) Lewis structure of CO_3^{2-} ion is

Formal charge on C atom $= 4 - 0 - \frac{1}{2}(8) = 0,$

Formal charge on double bonded O atom

$$= 6 - 4 - \frac{1}{2}(4) = 0$$

Formal charge on single bonded O atom

$$= 6 - 6 - \frac{1}{2}(\ ) = -1$$

(ii) Lewis structure of NO_2^- ion is $\left[:\overset{..}{O} = \overset{+}{\overset{..}{N}} - \overset{..}{O}: \right]^-$

Formal charge on N atom

$$= 5 - -\frac{1}{2}(6) = 0,$$

Formal charge on double bonded O atom

$$= 6 - 4 - \frac{1}{2}(4) = 0$$

Formal charge on single bonded O atom

$$= 6 - 6 - \frac{1}{2}(\ ) = -1$$

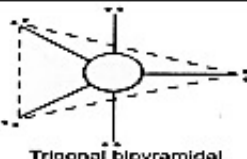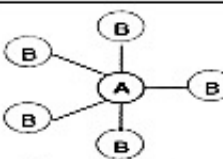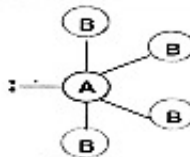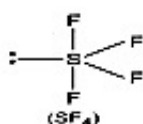**Significance of formal charge.** The main advantage of the calculation of formal charges is that it helps to select the most stable structure, i.e., the one with least energy out of the different possible Lewis structures. The most stable is the one which has the smallest formal charges on the atoms.

7. LIMITATIONS OF LEWIS-LANGMUIR CONCEPT OF COVALENT BOND

Lewis-Langmuir concept of covalent bond, as explained in ec. 4.8, has the following limitations :

(i) It could not explain how the atoms are held together in the molecules like H_2, Cl_2 etc. in which there are no ions and hence there are no electrostatic forces of attraction, i.e., it could not explain the formation of a covalent bond.

(ii) It could not explain the shapes of molecules containing covalent bonds.

(iii) It could not explain the release of energy during the formation of a covalent bond.

8. VALENC SHEELL ELECTRON PAIR REPULSION THEORY

The first simple theory that was put forward to explain the shapes of molecules is known as Valence Shell. Electron Pair Repulsion (VSEPR) theory. This theory was given by Sidgwick and Powell in 1940 and was further improved by Nyholm and Gillespie in 1957.

The electron pairs surrounding the central atom repel one another and move so far apart from one another that there are no further repulsions between them. As a result, the molecule has minimum energy and maximum stability.

Table : Shapes (Geometry) of molecules containing bond pairs only or bond pairs and lone pairs

Total No. of electron pairs	Geometry of the electron pairs	Bond pairs	Lone pairs	Geometry (Shape) of the molecule	Illustrative Example (Other Examples)
		(Molecular Formula)			
2	Linear	2	0	Linear	$\ddot{O}=C=\ddot{O}$ (BeF$_2$, BeCl$_2$, HgCl$_2$)
		(AB$_2$)			
3	Triangular planar	3	0	Triangular planar	(AlCl$_3$, SO$_3$)
		(AB$_3$)			
		2	1	Bent (V-shape)	(SO$_2$, O$_3$, SnCl$_2$)
		(AB$_2$L)			
4	Tetrahedral	4	0	Tetrahedral	(SiF$_4$, NH$_4^+$)
		(AB$_4$)			
		3	1	Trigonal pyramidal	(PCl$_3$, NCl$_3$, NF$_3$, PH$_3$, H$_3$O$^+$)
		(AB$_3$L)			
		2	2	Bent	(H$_2$S, NH$_2^-$)
		(AB$_2$L$_2$)			
5	Trigonal bipyramidal	5	0	Trigonal bipyramidal	PCl$_6$ (PF$_5$, SbCl$_5$, AsF$_5$)
		(AB$_5$)			
		4	1	See saw	(SF$_4$)
		(AB$_4$L)			

CHEMICAL BONDING

		3	2 (AB$_3$L$_2$)	T-shaped	(ClF$_3$)
		2	3 (AB$_2$L$_3$)	Linear	XeF$_2$ (I$_3^-$, Br$_3^-$, ICl$_2^-$)
6	Octahedral	6	0 (AB$_6$)	Octahedral	SF$_6$
		5	1 (AB$_5$L)	Square pyramidal	ClF$_5$ (IF$_5$, BrF$_5$)
		4	2 (AB$_4$L$_2$)	Square planar	XeF$_4$

8.1 Calculation of total number of electron pairs, bond pairs and lone pairs and predicting the shapes of the molecules and ions.

(i) Total no. of electron pairs around the central atom

$$= \frac{1}{2} \text{ (No. of valence electrons of central atom +}$$

No. of atoms linked to central atom by single bonds)

For negative ions, add number of electrons equal to the units of negative charge on the ion to the valence electrons of the central atom.

For positive ions, subtract number of electrons equal to the units of positive charge on the ion from the valence electrons of the central atom.

(ii) No. of bond pairs (shared pairs) = No. of atoms linked to central atom by single bonds.

(iii) No. of lone pairs = Total no. of electron pairs – No. of shared pairs.

Example

On the basis of VSEPR theory, predict the shapes of the following :

(i) ClF$_3$ (ii) BrF$_5$

Sol. (i) Shape of ClF$_3$

No. of valence electrons of the central Cl atom = 7

No. of atoms linked to it by single bonds = 3.

∴ Total no. of electron pairs around Cl $= \dfrac{7+3}{2} = 5$

No. of bond pairs = No. of atoms linked to Cl = 3.

∴ No. of lone pairs = 5 – 3 = 2.

Thus, the molecule is of the type AB$_3$L$_2$.

Hence, it is T-shaped.

(ii) Shape of BrF$_5$

No. of valence electrons of central Br atom = 7

No. of atoms linked to it by single bonds = 5.

∴ Total no. of electron pairs around Br $= \dfrac{7+5}{2} = 6$

No. of bond pairs = No. of atoms linked to Br = 5.

∴ No. of lone pairs = 6 – 5 = 1.

Thus, the molecule is of the type AB$_5$L. Hence, it has square pyramidal shape.

9. HYBRIDISATION

Hybridisation is defined as the mixing of the atomic orbitals belonging to the same atom but having slightly different energies so that a redistribution of energy takes place between them resulting in the formation of new orbitals of equal energies and identical shapes. The new orbitals thus formed are known as hybrid orbitals.

Some Important Points about Hybridisation

(i) Only those orbitals which have approximately equal energies and belong to the same atom or ion can undergo hybridisation.

(ii) Number of hybrid orbitals produced is equal to the number of atomic orbitals mixed.

(iii) It is not necessary that all the half-filled orbitals must participate in hybridisation. Similarly, it is not necessary that only half-filled orbitals should participate in hybridisation. Even completely filled orbitals with slightly different energies can also participate.

(iv) Hybridisation never takes place in isolated atoms but it occurs only at the time of bond formation.

(v) Type of hybridisation indicates the geometry of molecules. One can tell the shape of a molecule by knowing the kind of hybridisation involved.

(vi) The bigger lobe of the hybrid orbital always has +ve sign while the smaller lobe on the opposite side has a -ve sign.

9.1 Type of Hybridisation

1. **Diagonal or sp hybridisation**

When one s and one p orbital belonging to the same main shell of an atom mix together to form two new equivalent orbitals, the type of hybridisation is called sp hybridisation or diagonal hybridisation. The new orbitals formed are called sp hybrid orbitals.
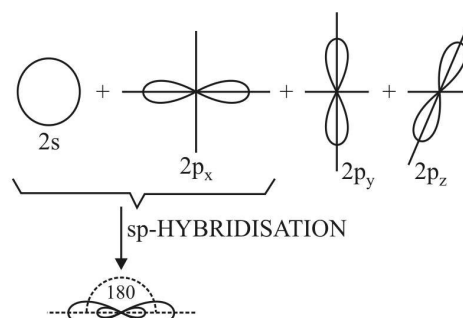
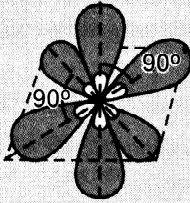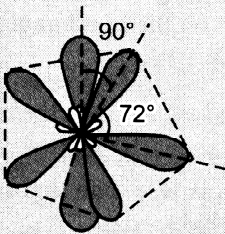sp-HYBRIDISATION

TWO sp-HYBRID ORBITALS

2. **Trigonal or sp^2 hybridisation**

When one s and two p orbitals of the same shell of an atom mix to form three new equivalent orbitals, the type of hybridisation is called sp^2 hybridisation or trigonal hybridisation. The new orbitals formed are called sp^2 hybrid orbitals.
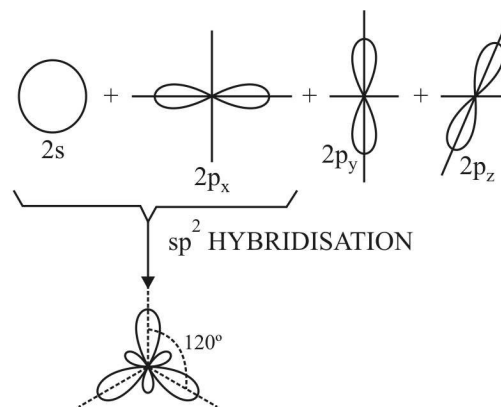
sp^2 HYBRIDISATION

THREE sp^2 HYBRID ORBITALS

Types of Hybridisation	Atomic orbitals Involved	Representing directions of hybrid orbitals formed along with bond angles	Shape of the molecule	Examples
1. sp	one s + one p	180°	Linear	$BeCl_2$, BeH_2, C_2H_2, $HgCl_2$
2. sp^2	one s + two p	120°	Triangular planar	BF_3, BCl_3, C_2H_4, NO_3^-, CO_3^{2-}
3. sp^3	one s + three p	109° 28'	Tetrahedral	CH_4, CCl_4, $SnCl_4$, NH_4^+
4. dsp^2	one d ($d_{x^2-y^2}$) +one s + two p	90°	Square planar	$[Ni(CN)_4]^{2-}$, $[PtCl_4]^{2-}$
5. sp^3d	one s + three p + one d (d_{z^2})	90° 120°	Trigonal bipyramidal	PF_5, PCl_5

Types of Hybridisation	Atomic orbitals involved	Representing directions of hybrid orbitals formed along with bond angles	Shape of the molecule	Examples
6. sp^3d^2 or d^2sp^3	one s + three p + two d ($d_{x^2-y^2}$ and d_{z^2})		Octahedral	SF_6, $[CrF_6]^{3-}$, $[Co(NH_3)_6]^{3+}$
7. sp^3d^3	one s + three p + d_{xy}, d_{yz}, d_{xz}		Pentagonal bipyramidal	IF_7

9.2 Predicting Hybridisation

(a) Predicting hybridisation

Calculate the number of hybrid orbitals (X) to be formed by the central atom as follows :

$$X = \frac{1}{2}\left[\left\{\begin{array}{l}\text{No. of valence electrons}\\\text{of the central atom}\end{array}\right\}\right] +$$

$$\left\{\begin{array}{l}\text{No. of monovalen atoms / groups}\\\text{surrounding the central atom}\end{array}\right\} - \left\{\begin{array}{l}\text{Charge on the cation}\\\text{if the given species is}\\\text{a polyatomic cation}\end{array}\right\}$$

$$+ \left\{\begin{array}{l}\text{Charge on the anion}\\\text{if the given species is}\\\text{a polyatomic anion}\end{array}\right\}$$

i.e., $X = \frac{1}{2}[VE + MA - c + a]$

Note that only monovalent atoms (MA) or groups are to be considered. For divalent ions, MA = 0.

If X = 2, it means two hybrid orbitals are to be formed. Hence, hybridization is sp. If X = 3, it means three hybrid orbitals are to be formed. Hence, hybridisation is sp^2 and so on, as given in the following table :

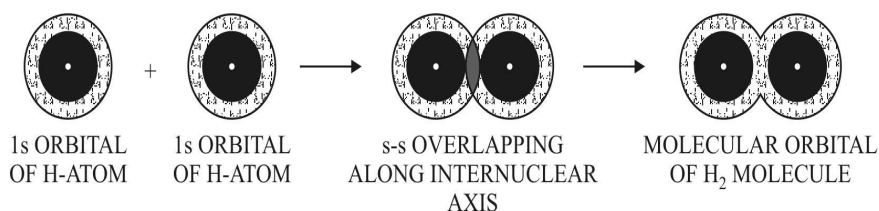| Value of X	2	3	4	5	6	7
Type of hybridisation	sp	sp^2	sp^3	sp^3d	sp^3d^2	sp^3d^3

10. VALENCE BOND THEORY

10.1 Types of covalent bond

Depending upon the type of overlapping, the covalent bonds are mainly of two types :
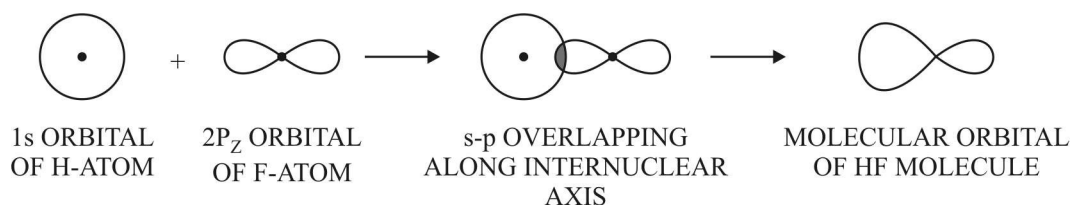
1. Sigma (σ) bond

When a bond is formed between two atoms by the overlap of their atomic orbitals along the internuclear axis (end to end or head on overlap), the bond formed is called sigma (σ) bond.
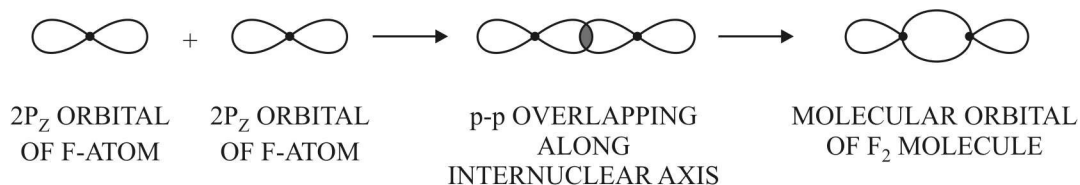
(i) s-s overlapping

1s ORBITAL OF H-ATOM + 1s ORBITAL OF H-ATOM → s-s OVERLAPPING ALONG INTERNUCLEAR AXIS → MOLECULAR ORBITAL OF H_2 MOLECULE

(ii) s-p overlapping

| 1s ORBITAL OF H-ATOM | 2P_Z ORBITAL OF F-ATOM | s-p OVERLAPPING ALONG INTERNUCLEAR AXIS | MOLECULAR ORBITAL OF HF MOLECULE |

(iii) p-p overlapping

| 2P_Z ORBITAL OF F-ATOM | 2P_Z ORBITAL OF F-ATOM | p-p OVERLAPPING ALONG INTERNUCLEAR AXIS | MOLECULAR ORBITAL OF F_2 MOLECULE |

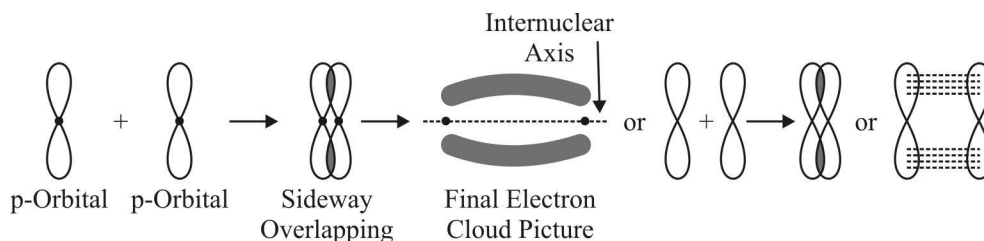**2. Pi (π) Bond**

Pi-bond is formed by lateral (sideways) overlapping of p-orbitals, i.e., by overlapping of p-orbitals in a direction at right angles to the internuclear axis (figure).

p-p overlapping forming a pi bond

(i) In case of oxygen molecule (each oxygen atom having electronic configuration, $1s^2\,2s^2\,2p_x^2\,2p_y^1\,2p_z^1$), the two atoms are held together by one σ-bond and one π-bond as shown in figure.
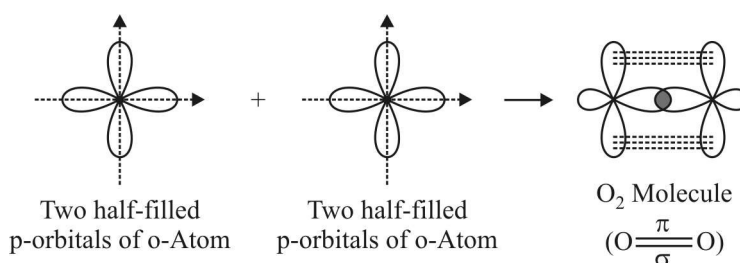
Formation of oxygen molecule

Table : Comparison and sigma and pi bonds

Sigma (σ) Bond	Pi (π) Bond
(i) This bond is formed by overlap of orbitals along their internuclear axis (end to end overlap).	(i) This is formed by sideway overlapping of orbitals (lateral overlapping).
(ii) This is formed by overlapping between s-s, s-p or p-p orbitals.	(ii) This is formed by the overlap of p-p orbitals only.
(iii) Overlapping is quite large and hence sigma bond is a strong bond.	(iii) Overlapping is to a small extent. Hence, π-bond is a weak bond.
(iv) Electron cloud in this case is symmetrical about the line joining the two nuclei.	(iv) Electron cloud of π-bond is unsymmetrical.
(v) Sigma bond consists of only one electron cloud, symmetrical about the internuclear axis.	(v) Pi (π) bond consists of two electron clouds, one above the plane of atomic nuclei and the other below it.
(vi) Free rotation about a σ-bond is possible.	(vi) Free rotation about a π-bond is not possible because on rotation, overlapping vanishes and so the bond breaks.

10.2 Bond Parameters

10.2.1 Bond length

The equilibrium distance between the centres of the nuclei of the two bonded atoms is called its bond length.

10.2.1.1 Factors affecting bond length

(i) Size of the atoms : The bond length increases with increase in the size of the atoms. For example, bond lengths of H–X are in the order :

HI > HBr > HCl > HF

(ii) Multiplicity of bond : The bond length decreases with the multiplicity of the bond. Thus, bond length of carbon-carbon bonds are in the order :

$C \equiv C < C = C < C - C$

(iii) Type of hybridisation (discussed later in sec. 4.24). As an s-orbital is smaller in size, greater the s-character, shorter is the hybrid orbital and hence shorter is the bond length. For example,

Bond lengths : sp^3 C–H > sp^2 C–H > sp C–H

s-character :   (25%)   (33%)   (50%)

10.2.2 Bond energy

The amount of energy required to break one mole of bonds of a particular type so as to separate them into gaseous atoms is called bond dissociation enthalpy or simply bond enthalpy.

10.2.2.1 Factors affecting Bond energy

(i) Size of the atoms : Greater the size of the atoms, greater is the bond length and less is the bond dissociation enthalpy, i.e., less is the bond strength.

(ii) Multiplicity of bonds : For the bond between the same two atoms, greater is the multiplicity of the bond, greater is the bond dissociation enthalpy. This is firstly because atoms come closer and secondly, the number of bonds to be broken is more. For example, bond dissociation enthalpies of H_2, O_2 and N_2 are in the order :

$H–H < O = O < N \equiv N$

(iii) Number of lone pairs of electrons present : Greater the number of lone pairs of electrons present on the bonded atoms greater is the repulsion between the atoms and hence less is the bond dissociation enthalpy. For example, for a few single bonds, we have

Bond	C–C (in $H_3C–CH_3$)	N–N (in : N ≡ N :)	O–O (in :Ö — Ö:)	F–F (:F̈ — F̈:)
Lone pairs of electrons on each atom	0	1	2	3
Bond enthalpy (kJ mol^{-1})	348	163	146	139

10.2.3 Bond angle

The angle between the lines representing the directions of the bonds, i.e., the orbitals containing the bonding electrons is called the bond angle.
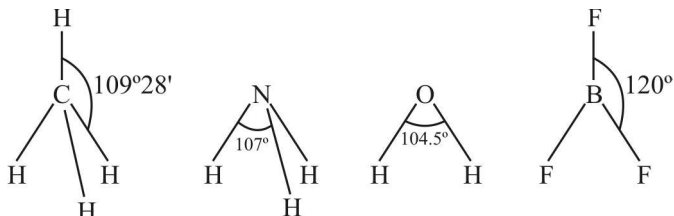
10.2.4 Bond order

In the Lewis representation of a molecule or ion, the number of bonds present between two atoms is called bond order. For example, the bond orders of a few molecules are given below :

Molecule : H—H   O = O   N ≡ N   C ≡ O

Bond order :   1   2   3   3

For odd electron molecules, as the three electron bond is considered as equivalent to half covalent bond, bond order can be fractional also. For example, Lewis structure of NO is

$:N\overset{\bullet\bullet\bullet}{=\!=}O:$.

11. MOLECULAR ORBITAL THEORY

There is another approach to chemical bonding known as molecular orbital theory (MOT) developed by **Mulliken** (1932) and **Hund**, which explains the bonding characteristics in a better way. The molecular orbital theory considers the entire molecule as a unit with all the electrons moving under the influence of all the nuclei present in the molecular. This approach recognizes that each electron belongs to the molecule as a whole and may move within the entire molecule.

11.1 Molecular Orbitals

When the atoms to be bonded come close together, the orbitals of the bonded atoms lose their individual character and fuse (overlap) to form larger orbitals called molecular orbitals. Like atomic orbitals, there are molecular orbitals in a molecule. The only difference is that in atomic orbitals, electrons move under the influence of only one nucleus (i.e. Atomic orbital are monocentric), while in molecular orbitals, electrons move under the influence of many nuclei, they are polycentric.

11.2 Important features of M.O.T.

(i) Like an Atomic orbital which is around the nucleus of an atom there are molecular orbital which are around the nuclei of a molecule.

(ii) The molecular orbitals are entirely different from the atomic orbitals from which they are formed.

(iii) The valence electrons of the constituent atoms are considered to be moving under the influence of nuclei of participating atoms in the molecular orbital.

(iv) The molecular orbitals possess different energy levels like atomic orbitals in an isolated atom.

(v) The shape of molecular orbitals are dependent upon the shapes of atomic orbitals from which they are formed.

(vi) Molecular orbitals are arranged in order of increasing energy just like atomic orbitals.

(vii) The number of molecular orbitals formed is equal to the number of atomic orbitals combining in bond formation.

(viii) Like atomic orbitals, the filling of electrons in molecular orbitals is governed by the three principles such as **Aufbau principle, Hund's rule and Pauli's exclusion principle.**

11.3 Conditions for atomic orbitals to form M.O.
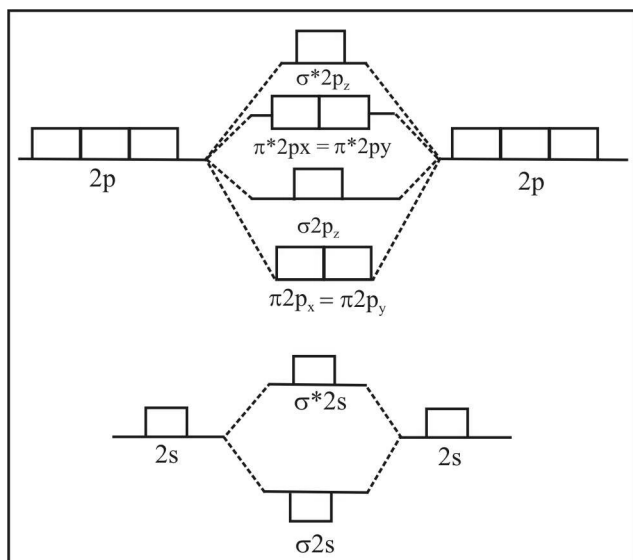
(i) The combining A.O. should be of a comparable energy.

(ii) The combining atomic orbitals must overlap to a large extent greater the overlap, stable is the molecule formed.

11.4 Relative energies of M.O. and filling of electron

Energy diagram is shown below
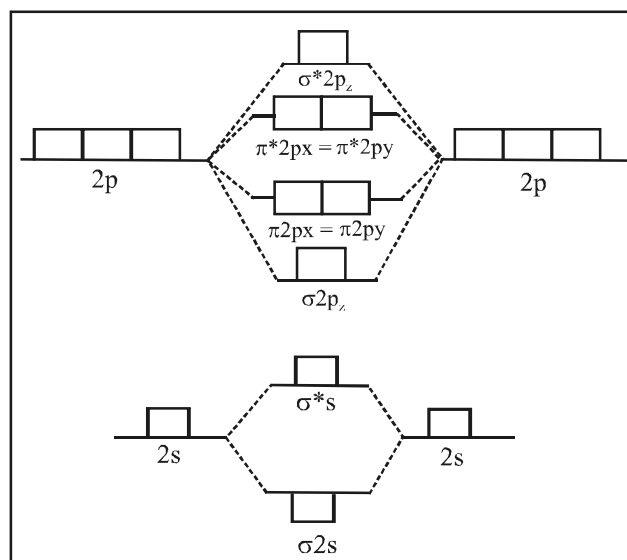

M.O Energy level diagram for O_2, F_2 and Ne.

M.O energy diagram for Li$_2$, Be$_2$, B$_2$, C$_2$ and N$_2$ molecule

12. METALLIC BOND

The constituent particles of metallic solids are metal atoms which are held together by metallic bond. A metal atom is supposed to consit of two parts, valence electrons and the remaining part (the neucleus and the inner shells) called **kernel.** The kernels of metal atoms occupy the lattice sites while the space between the kernel is occupied by valence electrons. Due to small ionisation energy the valence electrons of metal atoms are not held by the nucleus firmly. Therefore, the electrons leave the field of influence of one kernel and come under the influence of another kernel. Thus the electrons are not localised but are mobile. The simultaneous attraction between the kernels and the mobile electrons which hold the kernel together is known as **metallic bond.** This model is known electron sea model.

13. HYDROGEN BONDING

When a hydrogen atom linked to a highly electronegative atom (like F,O, or N) comes under the influence of another strongly electronegative atom, then a weak bond is developed between them which is called as **hydrogen bond.** It is represented by dotted line as follows

$$\overset{+\delta}{H}—\overset{+\delta}{X}----\overset{+\delta}{H}—\overset{-\delta}{X}----\overset{+\delta}{H}—\overset{-\delta}{X}$$
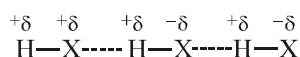
As a result of hydrogen bonding, a H–atom links the two electronegative atoms simultaneously, one by a covalent bond and the other by a hydrogen bond. Hence it is said to form a hydrogen bridge. It is merely a strong electrostatic attractive forces and not a normal chemical bond. It is very weak (strength about 2-10 K cal/mol).

13.1 Conditions for Hydrogen bonding

(a) The molecule must contain a highly electronegative atom linked to H-atom. The higher the electronegativity, more is the polarisation of the molecule.

(b) The size of the electronegative atom should be small. The smaller the size the greater is the electrostatic attraction.

13.2 Types of Hydrogen bonding

13.2.1 Intermolecular Hydrogen bonding

When hydrogen bonding takes place between different molecules of the same or different compounds, it is called intermolecular hydrogen bonding e.g. HF, H$_2$O, ROH (same compound) water-alcohol, water ammonia (different compound) etc.

$$\overset{+\delta}{H}—\overset{-\delta}{O}-----\overset{+\delta}{H}—\overset{-\delta}{O}-----H—O-----\overset{+\delta}{H}—\overset{-\delta}{O}$$
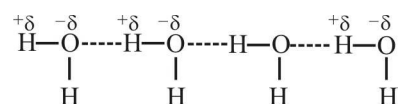
13.2.2 Intramolecular hydrogen bonding

The hydrogen bonding which takes place within a molecule itself. It takes place in compounds containing two groups such that one group contain a H-atom linked to an electronegative atom and the other group contains a highly electronegative atom linked to a lesser electronegative atom. The bond is formed between the H-atom of one group with the more electronegative atom of the other group.

Examples are as shown below

**O-Nitrophenol**   **O-Niholeny aldehyde**
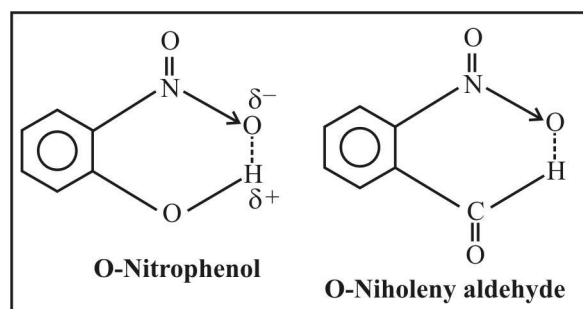
14. VANDER WAAL'S FORCES

(a) This type of attractive forces occurs in case of non polar molecules such as H$_2$, O$_2$, Cl$_2$, CH$_4$, CO$_2$, etc.

(b) The existence of weak attractive forces among the nonpolar molecule was first proposed by Dutch scientist **J.D. Vander Waal.**

(c) Vander waal force $\propto$ molecular weight

$\propto$ Boiling point

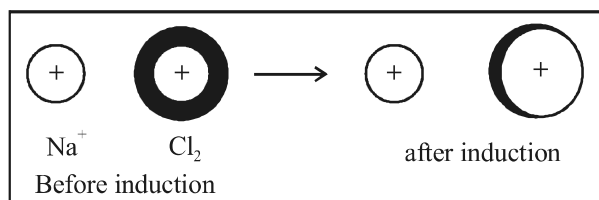### 14.1 Types of Vander Waal's force

14.1.1 Ion dipole attraction - This force is between an ion such as Na^+ and a polar molecule such as HCl
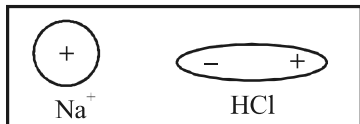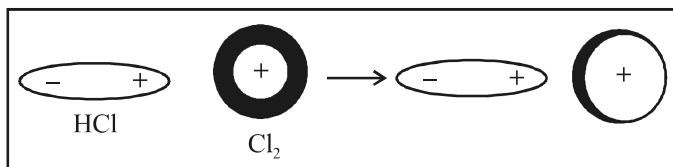

14.1.2 Dipole dipole attraction - It is again in between two polar molecules such as HF and HCl
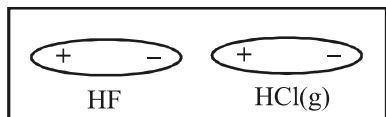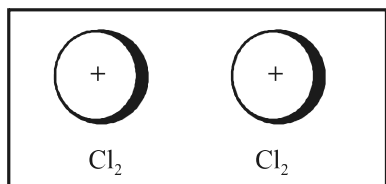

14.1.3 Ion induced dipole attraction - In this case a neutral molecule is induced by an ion as a dipole as shown in fig

14.1.4 Dipole - induced dipole attraction : In this case a neutral molecule is induced as a dipole by another dipole as show in fig

14.1.5 Induced dipole - induced dipole attraction or London dispersion force between two non polar molecules as in Cl_2, He etc.

NOTE

The relative strength of various bonds is as follows :

Ionic bond > Covalent bond > Metallic bond > H-bond > Vander waal bond.

15. DIPOLE MOMENT

A molecule with positive and negative charge centres in equilibrium is called as dipole and is characterised by possessing a quantity dipole moment (μ) defined as the product of the magnitude of charge (q) and the distance (d) separating the centres of +ve and –ve charges. Its direction is from +ve end to – ve end.

$$\mu = q \times d$$

The charge q on an electron is 4.8×10^{-10} esu. The distance is measured in cm and is of order of 1 Å, i.e., 10^{-8} cm. Its unit in CGS system is debye (D).

A molcule will have a dipole moment of 1 Debye (D) if charges of 1×10^{-8} esu are separated by a distance of 1Å.

Thus, $1D = 1 \times 10^{-18}$ esu. cm.

Applications of Dipole Moment

(i) The molecules having zero moment are non-polar molecules and those having $\mu_{net} \neq 0$ are polar in nature.

(ii) The value of dipole moment can be used for determining the amount of ionic character in a bond.

Percentage of ionic character

$$= \frac{\text{Experimental value of dipole moment}}{\text{Theoretical value of dipole moment}} \times 100$$

SOLVED EXAMPLES

Example - 1

Which of the following compounds has the largest dipole moment ?

(i) CH_3OH   **(ii) CH_4**

(iii) CF_4   **(iv) CO_2**

(v) CH_3F.

Sol. CH_4 and CF_4 have tetrahedral structure and are symmetrical, hence their dipole moment is zero, CO_2 is linear and hence its dipole moment is also zero of the remaining CH_3OH and CH_3F, since F is more electronegative than O, CH_3F will have high dipole moment.

Example - 2

What type of bond is formed when atoms have

(i) Zero difference of electronegativity.

(ii) Little difference of electronegativity.

(iii) High difference of electronegativity.

Sol. (i) Non-polar covalent

(ii) Polar covalent

(iii) Electro-valent.

Example - 3

Explain the formation of a chemical bond.

Sol. A chemical bond is formed by mutual sharing or by transfer of one or more electrons. In doing so, each combining atom acquires stable noble gas electronic configuration having 8 electrons in its outermost shell.

Example - 4

Why NH_3 has higher dipole moment than NF_3 ?

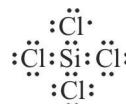**Sol.** In NH_3 dipoles are towards lone pair whereas in NF_3 dipoles A are opposite to lone pair of electrons.
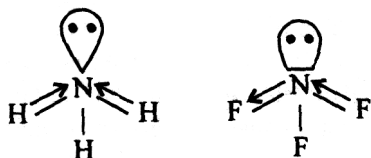
Example - 5

Draw the Lewis structures for the following molecules and ions :

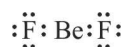**H_2S, $SiCl_4$, BeF_2, CO_3^{2-}, HCOOH.**

Ans. H_2S H $:\ddot{S}:$ H
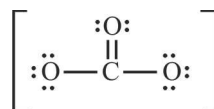
$SiCl_4$

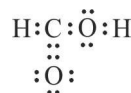BeF_2 $:\ddot{F}: Be :\ddot{F}:$

CO_3^{2-}

HCOOH

Example - 6

Write the favorable factors for the formation of ionic bond.

Sol. Factors which favour the formation of ionic bond :

(i) **Low ionisation energy :** In the formation of ionic bond a metal atom loses electron to form cation. This process requires energy equal to the ionisation energy. Lesser the value of ionisation, greater will be the tendency of the atom to form cation.

(ii) **High electron affinity :** The value of electron affinity gives the tendency of an atom to form anion. Greater the value of electron affinity, more will be the tendency of an atom to form anion.

(iii) **High lattice energy :** The lattice energy should be high so that it overcomes the apparent deficit of energy of absorption, that is, sublimation energy, ionization energy, dissociation energy and second affinity. Higher the lattice energy, greater will be the ease of formation of the ionic compound.

The magnitude of lattice energy gives an idea about the interionic forces. It depends upon the following factors :

(a) **Size of the ions :** Smaller the size of the ions, lesser is the inter-nuclear distance. Consequently, the interionic attractions will be high and the lattice energy will also be large.

(b) **Charge on the ions :** Larger the magnitude of charge on the ions, greater will be the attractive forces between the ions. Consequently, the lattice energy will be high.

Example - 7

Discuss the shape of the following molecules using the VSEPR model.

$BeCl_2$, BCl_3, $SiCl_4$, AsF_5, H_2S, PH_3.
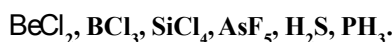
Sol. **$BeCl_2$:** A linear molecule. Be atom has 2 electrons in it outermost orbit. Each chlorine atom has seven valence electrons. The Lewis structure of $BeCl_2$ is

$$\cdot Be \cdot + 2 \cdot \ddot{\underset{..}{Cl}} : \longrightarrow : \ddot{\underset{..}{Cl}} \cdot \cdot Be \cdot \cdot \ddot{\underset{..}{Cl}} : \longrightarrow Cl-Be-Cl$$

There are two electrons pairs and to minimise the repulsion, these electron pairs tend to keep themselves far away from each other, i.e., 180º apart. This gives $BeCl_2$ a linear structure.

BCl_3 : In BCl_3 molecule, the three bond pairs of electrons are located around B in a triangular arrangement. Thus, the molecule BCl_3 has a **triangular planar geometry.**
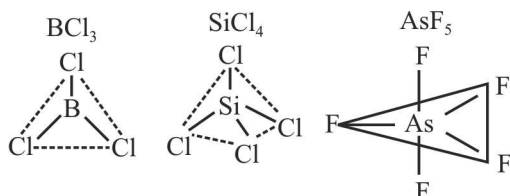
$SiCl_4$: A tetrahedral molecule. Si has 4 electrons in its outermost shell. Due to mutual sharing of electrons with Cl there are 4 electron pairs around Si. To keep the repulsion at the minimum, these 4 electron pairs should be arranged in a tetrahedral manner around Si. Thus, $SiCl_4$ is a tetrahedral molecule.

AsF_5 : Trigonal bipyramidal molecule : As has five electrons in its outermost orbit. Due to sharing of 5 electrons from 5 F-atoms, there are in all 5 electron pairs. These are distributed in space to form a trigonal bypyramid.

H_2S : Bent (V-shaped) structure : S has 6 electrons its outermost shell. 2H-atoms contribute 2 electrons during bonding. Thus, there are 8 electrons or 4 electron pairs around S. This gives a tetrahedral distribution of electron pairs around S. The two corners of the tetrahedron are occupied by H-atoms and the other two by the lone-pairs of electrons. Thus, H_2S has a bent structure.
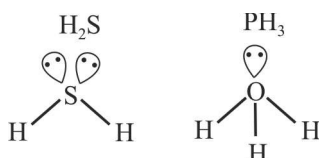

PH_3 : Trigonal pyramidal : Phosphorus atom has 5 electrons in its outermost orbit. H-atoms contribute one electron each to make in all 8 electrons around P-atom. Thus, 4 pairs of electrons would be distributed in a tetrahedral fashion around the central atom. Three pairs form three P-H bonds while the fourth pair remains unused. Due to repulsion between the bonding and lone pairs of electrons, the angle $H\hat{P}H$ is not exactly tetrahedral (109º 28′). The actual HPH angle is 93.3º. Thus PH_3 is a trigonal pyramidal molecule.

Example - 8

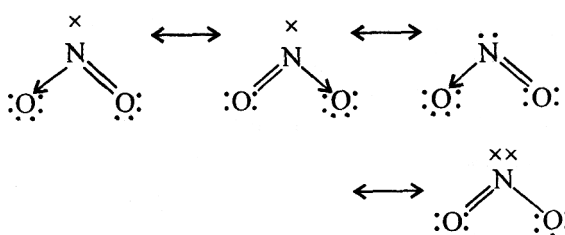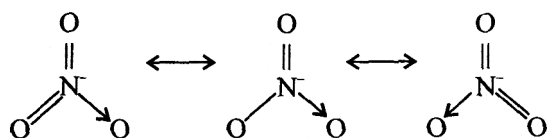**Write the resonance structures for SO_3, NO_2 and NO_3^-.**

Sol. (SO_3)
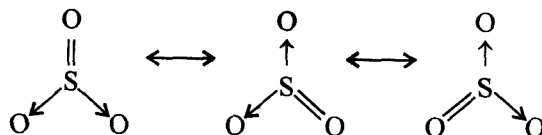
(NO)

(NO_3^-)

Example - 9

Arrange the following in order of decreasing bond angle, giving reason

$$NO_2, NO_2^+, NO_2^-$$

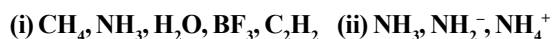**Ans.** $NO_2^+ > NO_2 > NO_2^-$. This is because NO_2^+ has no lone pair of electrons (i.e. has only bond pairs on two sides) and hence it is linear. NO_2 has one unshared electron while NO_2^- has one unshared electron pair. There are greater repulsions on N–O bonds in case of NO_2^- than in case of NO_2.
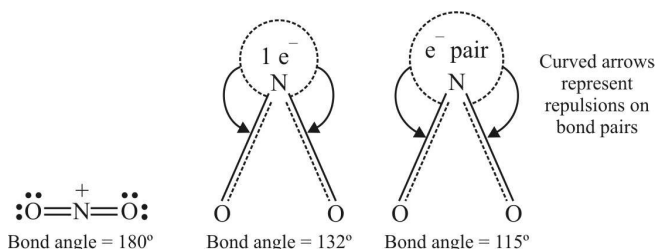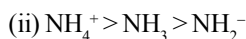

Example - 10

Arrange the following in order of decreasing bond angles

(i) CH_4, NH_3, H_2O, BF_3, C_2H_2 (ii) NH_3, NH_2^-, NH_4^+

Sol. (i) $C_2H_2 (180º) > CH_4 (109º 28′) > BF_3 (120º) >$

$NH_3 (107º) > H_2O > (104.5º)$

(ii) $NH_4^+ > NH_3 > NH_2^-$

This is because all of them involve sp^3 hybridization. The number of lone pair of electrons present on N-atom are 0, 1 and 2 respectively. Greater the number of lone pairs, greater are the repulsions on the bond pairs and hence smaller is the angle.

Example - 11

Which of the following species have same shape/same bond order ?

$$N_3^-, NO_2^-, CO_2, O_3$$
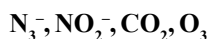
Sol. Isoelectronic species have same shape/same bond order. The number of outer electrons is same in CO_2 and N_3^- and same in O_3 and NO_2^-.

Example - 12

Although both CO_2 and H_2O are triatomic molecules, the shape of H_2O molecule is bent while that of CO_2 is linear, Explain this on the basis of dipole moment.

Sol. The H_2O molecule has a dipole moment of 1.84 D. There are two OH bonds in H_2O molecule. The O–H bonds are polar and has dipole moment of 1.5 D. Since the water molecule has a net dipole, hence the two O–H dipoles are not in a straight line opposing each other. This rules out the linear structure (H–O–H) for water. The two O–H bonds cannot lie along the same line in the same direction also. Therefore, the two O–H bonds in H_2O molecule must be inclined to each other at certain angle. Thus, H_2O molecule has an angular shape.

The CO_2 molecule has zero dipole moment. In CO_2, there are two C = O bonds. Each C = O bond is a polar bond. This means each bond has a dipole moment. Since, the net dipole, and hence the two bonds must be just opposite to each other, i.e., the two bonds must be at 180° relative to each other. Thus CO_2 is a linear molecule.

Example - 13

Is there any change in the hybridization of B and N atoms as a result of the following reaction ?

$$BF_3 + NH_3 \longrightarrow F_3B \leftarrow NH_3$$
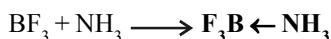
Sol. Here, B atom in BF_3 is sp^2 hybridized and one of its p orbital is empty. N in NH_3 is sp^3 hybridized and are of its hybrid orbitals is occupied by a lone-pair of electrons. During the reaction a coordinate bond is formed due to one-side sharing of electron pair.

$$BF_3 + NH_3 \longrightarrow [F_3B \leftarrow : NH_3]$$
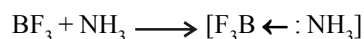
There is no change in the hybridization of any of the two atoms in this reaction.

Example - 14

Explain why BeH_2 molecule has a zero dipole moment although the Be-H bonds are polar.

Sol. This is because BeH_2 is a linear molecule and the two bond dipoles oriented at an angle of 180° neutralize each other. As a result, the net dipole moment of the molecule is zero.

$$H \underset{\longleftrightarrow}{\longrightarrow} Be \underset{\longleftrightarrow}{\longrightarrow} H$$
$$\mu = 0$$
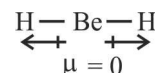
Example - 15

Describe the change in hybridization (if any) of the Al atom in the following reaction.

$$AlCl_3 + Cl^- \rightarrow AlCl_4^-$$

Sol. $AlCl_3 + Cl^- \rightarrow \underset{\substack{\text{tetrahedral geometry} \\ sp^3 \text{ hybridization}}}{AlCl_4^-}$

Aluminium chloride exists as dimer Al_2Cl_6. In this molecule chlorine atoms are arranged tetrahedrally around the two Al atoms.

Thus Al atoms show Sp^3 hybridisation in Al_2Cl_6. Thus, there is no change in the hybridisation of Al atom in the given reaction.
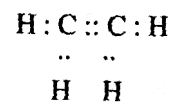
Example - 16

Draw diagrams showing the formation of a double bond and a triple bond between carbon atoms in C_2H_4 and C_2H_2 molecules.
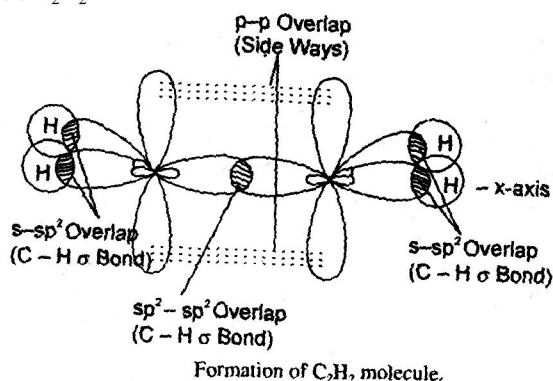
Sol. (i) C_2H_4
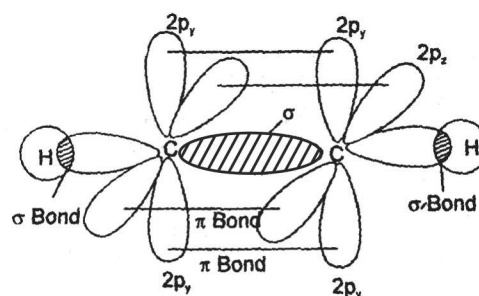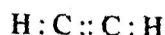

Formation of a double bond between carbon atoms in C_2H_4

The Lewis structure of ethylene is represented as

$$\text{H : C :: C : H}$$
$$\ddot{\text{H}} \quad \ddot{\text{H}}$$

(ii) C_2H_2

Formation of C_2H_2 molecule.

It is clear that the carbon-carbon triple bond is made up of one strong σ – bond and two weak π – bonds. The Lewis structure of acetylene can be represented as
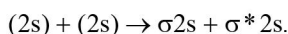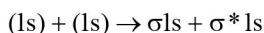
$$H : C :: C : H$$

Example - 17

Does Li_2 exist ? If so, estimate its bond order and compare its bond dissociation energy with that of H_2.

Sol. Li has a configuration : $1s^2, 2s^1$.

There are two s orbitals (1s and 2s) on each atom. These combine to give four MO's. These are

$$(1s) + (1s) \rightarrow \sigma 1s + \sigma * 1s$$

$$(2s) + (2s) \rightarrow \sigma 2s + \sigma * 2s.$$

Thus all the six electrons are accommodated in these four orbitals. The electronic configuration for Li_2 is $(\sigma 1s)^2 (\sigma * 1s)^2 (\sigma 2s)^2$.

$$N_b = 4, N_a = 2.$$

Bond order in $Li_2 = \dfrac{4-2}{2} = 1$.

Therefore, Li_2 should be a stable species. Its bond dissociation energy is 105 kJ mol^{-1}, as compared to 431 kJ mol^{-1} for H_2. Thus, the bond in Li_2 is much weaker than that on H_2. This is because 2s orbital of Li (involved in the bonding) is much larger than 1s orbital of H.

Example - 18

Explain how V.B theory differs from the Lewis concept.

Sol. The Lewis concept of describes the formation of bond in terms of sharing of one or more electron pairs and the octet rule. It does not explain the energetics of the bond formation and shapes of the polyatomic molecules.

The VB theory describes the bond formation in terms of hybridization and overlap of the orbitals. The overlap of orbitals along the intermolecular axis increases the electron-density between the two nuclei resulting in a decrease in the energy and formation of a bond.

Example - 19

Why is it that in the SF_4 molecule, the lone pair of electrons occupies and equatorial position in the overall trigonal bi-pyramidal arrangement in preference to an axial position.

Sol. In SF_4 molecule, the line pair of electrons occupies an equatorial position because in this geometry (sp^3d hybridisation), the line pair-bond pair repulsion is minimum
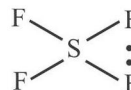
Example - 20

Define hydrogen bond. Is it weaker or stronger than the Van der Waals forces ?

Sol. The hydrogen bond can be defined as the attractive force which binds hydrogen atom of one molecule with the electronegative atom (F, O or N) of another molecule. A hydrogen bond is shown by a dotted line (.....)

Hydrogen bond is S t r o than the Van der Waals forces.

Example - 21

$NaNO_3$ on heating to 500°C decomposes to produce $NaNO_2$ and O_2, while the same salt on heating to 800°C, decomposes to Na_2O, N_2 and O_2. Explain in light of Fajan's rule.

Sol. The decomposition scheme can be shown as

$$NaNO_4 \xrightarrow{500°C} NaNO_2 + O_2$$
$$\downarrow 800°C$$
$$NaNO_3 \xrightarrow{800°C} Na_2O + N_2 + O_2$$
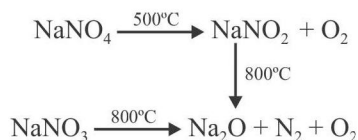
As we know tha thermal stability of a salt depends on percentage ionic character, $NaNO_2$ has greater ionic character than $NaNO_3$ because of lower polarizability of smaller nitrite ion than nitrate ion. Therefore, 500°C is sufficient for decomposition of less ionic $NaNO_3$ but $NaNO_2$ is stable at this temperature. On heating further to 800°C, the more stable $NaNO_2$ decomposes further to Na_2O and N_2, O_2.

Example - 22

Out of σ and π – bonds, **which one is stronger and why ?**

Sol. σ – bond is stronger. This is because σ – bond is formed by head-on overlapping of atomic orbitals and, therefore, the overlapping is large. π – bond is formed by sideway overlapping which is small.
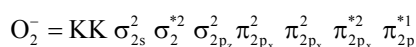
Example - 23

Out of p-orbital and sp-hybrid orbital which has greater directional character and why ?

Sol. sp-orbital has greater directional character than p-orbital. This is because p-orbital has equal sized lobes with equal electron density in both the lobes wheres sp-hybrid orbital has greater electron density on one side.
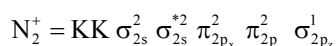
Example - 24

Compare the relative stabilities of O_2^- and N_2^+ and comment on their magnetic (paramagnetic or diamagnetic) behaviour.

Sol. M.O. Electronic configuration of

$O_2^- = KK\ \sigma_{2s}^2\ \sigma_2^{*2}\ \sigma_{2p_z}^2\ \pi_{2p_x}^2\ \pi_{2p_x}^2\ \pi_{2p_x}^{*2}\ \pi_{2p}^{*1}$

Bond order $= \dfrac{1}{2}(8-5) = \dfrac{3}{2} = 1.5$

M.O. Electronic configuration of

$N_2^+ = KK\ \sigma_{2s}^2\ \sigma_{2s}^{*2}\ \pi_{2p_x}^2\ \pi_{2p}^2\ \sigma_{2p_z}^1$

Bond order $= \dfrac{1}{2}(7-2) = \dfrac{5}{2} = 2.5$

As bond order of N_2^+ > bond order of O_2^-, therefore, N_2^+ is more stable than O_2^-.

Each of them contains unpaired electron, hence both are paramagnetic.

Example - 25

Explain why HF is less viscous than H_2O.

Sol. There is greater intermolecular hydrogen bonding in H_2O than that in HF as each H_2O molecule forms four H-bonds with other water molecules whereas HF forms only two H-bonds with other HF molecules. Greater the intermolecular H-bonding, greater is the viscosity. Hence, HF is less viscous than H_2O.

Example - 26

Write Lewis structure of the following compounds and show formal charge on each atom :

HNO_3, NO_2, H_2SO_4

Sol. $HNO_3 =$
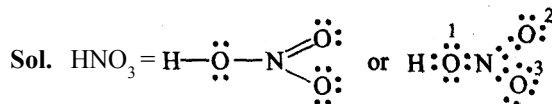
Formal charge $= V - L - \dfrac{1}{2}S$

Formal charge on H $= 1 - 0 - \dfrac{1}{2} \times 2 = 0$
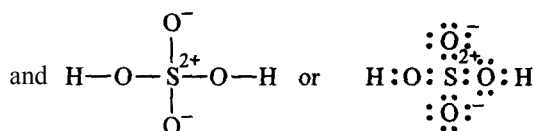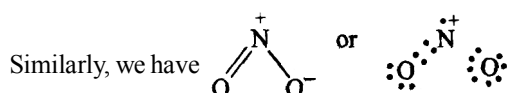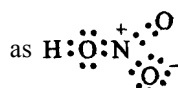
Formal charge on O (1) $= 6 - 4 - \dfrac{1}{2}(4) = 0$

Formal charge on N $= 5 - 0 - \dfrac{1}{2}(8) = 1$

Formal charge on O (2) $= 6 - 4 - \dfrac{1}{2}(4) = 0$

Formal charge on O (3) $= 6 - 6 - \dfrac{1}{2}(2) = -1$

Hence, we write the structure of HNO_3 with formal charges

as

Similarly, we have

and

Example - 27

What is mean by the term average bond ethalpy ? Why is there difference in bond enthalpy of O–H bond in ethanol (C_2H_5OH) and water ?

Sol. All the similar bonds in a molecule do not have the same bond enthalpies, e.g., in CH_4 , the four
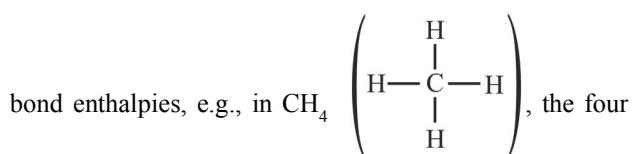
C–H bonds do not have the same bond enthalpies because after breaking of the bonds one by one, the electronic environment around carbon changes. Hence, the actual bond enthalpy of C–H bond is taken as the average value.

O–H bond in ethanol $\left(C_2H_5 - O\diagdown_H\right)$ and that in water

$\left(H - O\diagdown_H\right)$ do not have similar electronic environment around oxygen atom. Hence, their O–H bond enthalpies are different.

Example - 28

Write Lewis dot structures of the following molecules/ions :

(i) CO   **(ii) HCN**

Sol : V = number of valence electron of molecule

R = Number of electron required for octet in molecule

S = Number of shared electron (S = R – V)
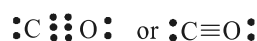
U = Number of unshared electron (U = V – S)

(i) CO

V = 4 + 6 = 10 electrons

R = 8 + 8 = 16 electrons

S = R – V = 6 electrons

U = 10 – 6 = 4 elctrons

:C :: O: or :C≡O:

(ii) HCN

V = 1 + 4 + 5 = 10 electrons

R = 2 + 8 + 8 = 18 electrons

S = 8 electrons

U = 2 electrons

H:C::N: or   H – C≡N:
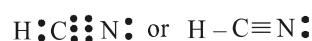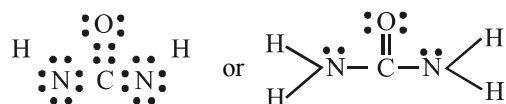
Example - 29

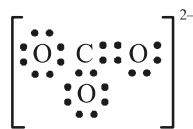**Write Lewis structures for**

(i) Urea, NH_2CONH

(ii) Carbonate ion, CO_3^{2-}.

Sol : **(i)** Urea, V = 24 electrons, R = 40 electrons, S = 16 electrons

U = 8 electrons

(ii) V = 24 electrons, R = 32 electrons, S = 8 electrons, U = 16 electrons.

$$\left[:O: \quad C :: O: \atop :O: \right]^{2-}$$

Example - 30

Arrange the following in increasing order of bond angle around the central atom :

$$BeF_2, BF_3, CH_4, NH_3, H_2O$$

Sol. $H_2O < NH_3 < CH_4 < BF_3 < BeF_2$

Bond angle   104.5º   106.5º   109º28'   120º   180º

Example - 31

Indicate the number of σ and π-bonds in the following molecules.

(i) $CH_3 - CH = CH_2$

(ii) $CH_3 - CH_2 - CH_2 - CH_3$

(iii) $CH_3 - C \equiv C - CH_3$

(iv)
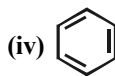
Sol.   For finding out the number of σ and π-bonds in a molecule, the following points should be kept in mind :

1. All single bonds are sigma bonds.

2. All double bonds consist of one σ and two π-bonds.

3. All triple bonds consist of one σ and two π-bonds.

(i) This molecule consists of seven single bonds and one double bond. Thus, number of σ-bonds = 8 and number of π-bonds = 1.

(ii) This molecule consists of 13 single bonds.

Thus, number of σ-bonds = 13.

(iii) This molecule consists of 8 single bonds and one triple bond. Thus, number of σ-bonds = 9 and number of π-bonds = 2.

(iv) The molecule of benzene consists of nine single bonds and three double bonds.

Thus, number of σ-bonds = 12 and number of π-bonds = 3.

Example - 32

Which of the two, peroxide ion or superoxide ion, has a larger bond length ?

Sol.   The bond length in a molecule depends on bond order. the higher the bond order, smaller will be the bond length.

Peroxide ion, O_2^{2-}

Configuration KK $\sigma(2s)^2 \overset{*}{\sigma}(2s)^2 \sigma(2p_z)^2 \pi(2p_x)^2$

$$\pi(2p_y)^2 \overset{*}{\pi}(2p_x)^2 \overset{*}{\pi}(2p_y)^2$$

Bond order $= \dfrac{8-6}{2} = 1$

Superoxide ion, O_2^-

Configuration KK $\sigma(2s)^2 \overset{*}{\sigma}(2s)^2 \sigma(2p_z)^2 \pi(2p_x)^2$

$$\pi(2p_y)^2 \overset{*}{\pi}(2p_x)^2 \overset{*}{\pi}(2p_y)^1$$

Bond order $= \dfrac{8-5}{2} = 1.5$

Bond order of superoxide is higher than peroxide ion, hence bond length of peroxide ion is larger.

Example - 33

Which of the following has maximum bond angle ?

H_2O, CO_2, NH_3, CH_4

Sol. CO_2 (Linear structure, carbon undergoes sp-hybridization).

Example - 34

Interpret the non-linear shape of H_2S molecule and non planar shape of PCl_3 using valence shell electron pair repulsion (VSEPR) theory.

Sol. In H_2S, two bonded pairs and two lone pairs of electrons are present, i.e., S undergoes sp^3-hybridization. Tetrahedral configuration comes into existence. Two of the positions are occupied by lone pairs, hence the actual structure is bent or V-shaped.

In PCl_3, three bonded pairs and one lone pair of electrons are present, i.e., P-atom undergoes sp^3– hybridization. Tetrahedral configuration comes into existence. One position is occupied by lone pair, hence the actual structure is pyramidal.

Example - 35

Hydrogen bonding does not exist in HCl through chlorine is quite electronegative.

Sol. This is due to the large size of Cl-atom

Example - 36

The dipole moment of KCl is 3.336×10^{-29} coulomb metre which indicates that it is a highly polarized molecule. The interatomic distance between K^+ and Cl^- in this molecule is 2.6×10^{-10} m. Calculate the dipole moment of KCl molecule, if there were opposite charges of one fundamental unit located at each nucleus. Calculate the percentage ionic character of KCl.

$\mu = q \times d$

Sol. q = one fundamental unit $= 1.062 \times 10^{-19}$ C

$d = 2.6 \times 10^{-10}$ M

$= 1.602 \times 10^{-19} \times 2.6 \times 10^{-10}$

$= 4.1652 \times 10^{-29}$ coulomb metre

Percentage ionic character

$$= \frac{3.336 \times 10^{-29}}{4.1652 \times 10^{-29}} \times 100 = 80.09$$

Example - 37

The correct order of the ionic character of PbF_2, $PbCl_2$, $PbBr_2$ and PbI_2 is :

(a) $PbF_2 > PbCl_2 > PbBr_2 > PbI_2$

(b) $PbF_2 > PbBr_2 > PbCl_2 > PbI_2$

(c) $PbF_2 < PbCl_2 < PbBr_2 < PbI_2$

(d) $PbF_2 < PbCl_2 > PbBr_2 > PbI_2$

Sol. Since the given dihalides contain the same cation viz Pb^{2+} but different anions (halide ions), the ionic character of these halides depends on the size of the halide ions. The ionic character decreases with the increases in the size of the halide ions. Thus since the size of halides ions increases as $F^- < Cl^- < Br < I$, the ionic character of $Pb X_2$ molecules decreases as $PbF_2 > PbCl_2 > PbBr_2 > Pb I_2$. Thus (a) is the correct answer.

Example - 38

Among the halides namely, NaF, NaCl, NaBr and NaI, NaF has the highest melting point, because NaF has :

(a) minimum ionic character

(b) maximum ionic character

(c) highest oxidising power

(d) lowest valency

Sol. Since the size of halide ions (X^-) increases as $F^- < Cl^- < Br^- < I^-$ the ionic character of MX molecules decreases as NaF > NaBr > NaI. Being the most ionic, NaF has the highest melting point.

Example - 39

A diatomic molecule has a dipole moment equal to 1.2 D. If its bond distance is 1.0 Å, what fraction of an electronic charge exists in each atom ?

(a) 12%   (b) 18%

(c) 25%   (d) 29%

Sol. Bond distance, $d = 1.0$ Å $= 1.0 \times 10^{-8}$ cm (given)

Dipole moment, $\mu = 1.2$ D $= 1.2 \times 10^{-18}$ esu. cm (given)

Electronic charge $= 4.8 \times 10^{-18}$ esu. cm (given)

Fraction of electronic charge $=$ x (to be calculated)

Now we know that :

$\mu = x \times d$

1.2×10^{-18} esu. cm $= x \times 10^{-8}$ cm

$\therefore \ x = \dfrac{1.2 \times 10^{-18} \text{ esu. cm}}{10^{-8} \text{ cm}} = 1.2 \times 10^{-10}$ esu

Out of 4.8×10^{-10} esu. cm electronic charge, the electronic charge existing on each atom $= 1.2 \times 10^{-10}$ esu

$\therefore$ Out of 100 esu. cm. electronic charge, the electronic charge existing on each atom

$= \dfrac{1.2 \times 10^{-10} \text{ esu}}{4.8 \times 10^{-10} \text{ esu. cm}} \times 100$

$= 25\%$

Example - 40

Which of the following tetraiodides is the least stable and has doubtful existence ?

(a) CI_4 (b) GeI_4

(c) SnI_4 (d) PbI_4

Sol. The given tetraiodides contain C, Ge, Sn and Pb as C^{4+}, Sn^{4+} and Pb^{4+} ions respectively. According to inert pair effect, the stability of these cations decreases as $C^{4+} > Ge^{4+} > Sn^{4+} > Pb^{4+}$. This order shows that since Pb^{4+} ion is the least stable, its tetraiodide, PbI_4 is also least stable and hence has doubtful existence.
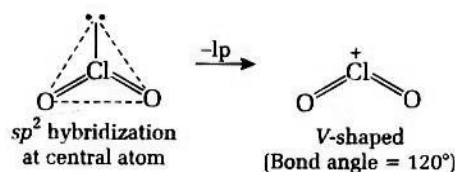
Example - 41

Discuss the bondings of ClO_2^+ ion.

Sol. The central atom is $Cl^{\bullet}$. The ions can be constituted as

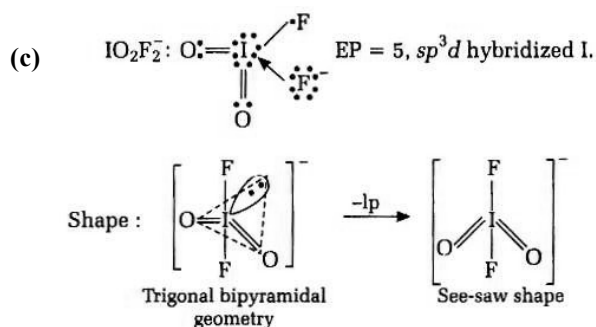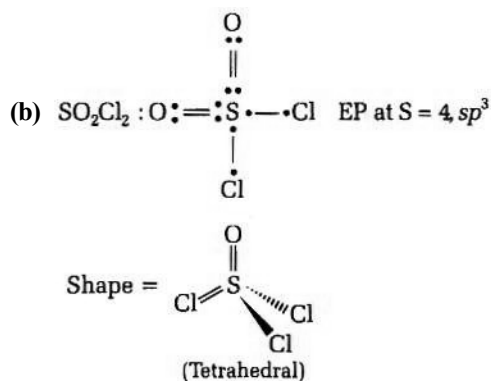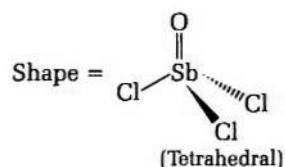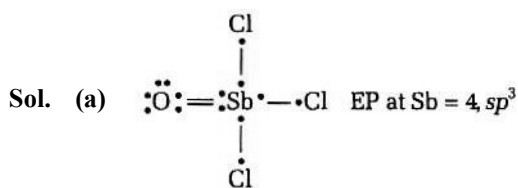EP at central atom $= 2(\sigma) + 1(lp) = 3$
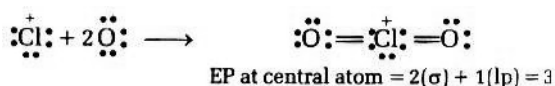
Geometry :

Example - 42

Write the Lewis dot formula of the following molecules and predict their molecular shapes :

(a) $OSbCl_3$ (b) SO_2Cl_2 (c) $IO_2F_2^-$

Sol. (a)

EP at Sb $= 4, sp^3$

Shape $=$

(Tetrahedral)

(b) SO_2Cl_2 :

EP at S $= 4, sp^3$

Shape $=$

(Tetrahedral)

(c) $IO_2F_2^-$:

EP $= 5, sp^3d$ hybridized I.

Shape :

Trigonal bipyramidal geometry → See-saw shape

Example - 43

> In vapour phase, phosphorus can exist as P_2 molecules, which is highly reactive, whereas N_2 is relatively inert, exaplain the difference.

Sol. Both P and N are from the same group (G15) of the Periodic Table, their diatomic molecule can be represented as :

$$\ddot{P}\!\!\equiv\!\!\ddot{P} \quad and \quad \ddot{N}\!\!\equiv\!\!\ddot{N}$$
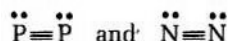
As we know, Pi-bonding between two phosphorus atoms is very unlikely due to larger atomic radius. Hence, diatomic P_2 is unstable but there is not such restriction of Pi-bonding to N and other second period elements.
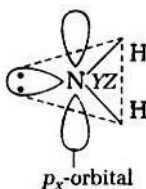
Example - 44

> Both NH_2^- and NH_2^+ are angular species but the bond angle in NH_2^- is less than that in NH_2^+. (a) What is the reason for this difference in bond angles ? (b) Take the x-axis as lying perpendicular to the molecular plane, does N ($2p_x$) orbital participate in the hybridization of either of species ?

Sol. (a) Hybridization at N atom is sp^3 in NH_2^- and sp^2 NH_2^+.

Therefore, bond angle in NH_2^- is close to 109° (tetrahedral angle), while bond angle in NH_2^+ is close to 120° (triangular planar angle).

(b) In NH_2^-, hybridization at N is sp^3 $\Rightarrow$ implies that all p-orbitals are involved in hybridization. In case of NH_2^+, the hybridization at N is sp^2 and the ion lies in YZ plane as X-axis lying in perpendicular plane. For the species to be in YZ plane, the two p-orbitals involved in sp^2 hybridization must be p_y and p_z orbitals i.e., $2p_x$ orbitals at N is remaining unhybridized as

p_x-orbital

Example - 45

> Although I_3^- is known, F_3^- is not. Explain.

Sol. In I_3^-, the central I is sp^3d hybridized and violate the octet rule. It is possible for elements of third and higher period to expand its valence shell beyond eight because they contain vacant d-orbitals. Hence formation of I_3^- is possible


sp^3d-hybridized
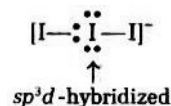
Since, fluorine is in second period, lack vacant d-orbitals, can't violate octet rule and, hence F_3^- does not exist.

Example - 46

> Iodine (I_2) is a volatile solid at room temperature and has very low solubility in water. However, I_2 is highly soluble in an aqueous solution of KI. Explain.

Sol. I_2 (s) being a molecular solids, the molecules are completely non-polar and covalent, have very low affinity for polar solvents like water. However, in solution of KI, I_2 forms forms KI_3 salt as

$$KI + I_2 \longrightarrow KI_3$$
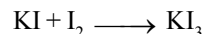
KI_3, a strongly ionic salt dissolves easily in water like other normal salts of the alkali metals. Hence, I_2 becomes soluble in KI via KI_3.

Example - 47

> Compare the F (axial) —A—F (equatorial) bond angles in these molecules. PF_6, SF_4 and ClF_3.

Sol. PF_5 is symmetrical trigonal bipyramidal molecule hence the sought bond angle is 90°.

SF_4 is a see-saw shaped molecule, while ClF_3 is T-shaped as shown below :
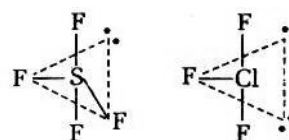
Axial bonds in SF_4 is repelled by one lone pair, the same in ClF_3 are repelled by two lone pairs, more repulsions are observed in ClF_3. Hence, F—S—F angle (axial-equatorial) is greater than F—Cl—F (axial-equatorial), although both are less than 90°. The order is : $PF_5 > SF_4 > ClF_3$.

**Example - 48**

> The Lewis structure of allene is
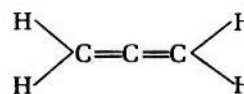
> Make a three dimensional sketch of this molecule and answer these questions : (a) Is the molecule planar ? (b) Does 1,3-dichloro propdience show geometrical isomerism ? (c) Is the molecule 1,3-dichloropropdiene polar ?

Sol. Hybridization of central carbon is sp and two of its

unhybridized p-orbitals are involved in Pi-bonding. Also p-orbitals at an atom are orthogonal (at 90º angle), the two Pi-bonds at central carbon are also orthogonal. Let these p-orbitals, involved in Pi-bondings, at central carbon by p_y and p_z, then
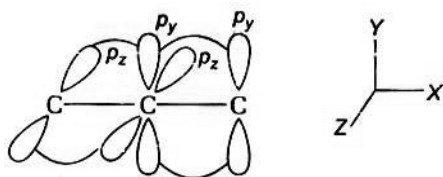
Hybridization at the terminal carbons are both sp^2. The two p-orbitals involved in sp^2 hybridization are p_x and p_y at left terminal and p_x and p_z at right terminals. Therefore, the three sp^2 hybrid orbitals at left terminal carbon are in xy plane, while the same at right terminal carbon are in xz plane. As a result, the two triangular planes at terminals are at right angles as shown below :
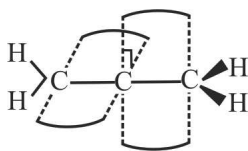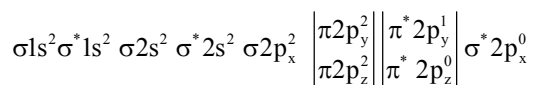

The two H—C—H planes at terminals are perpendicular to each other. (Pi-bonds are also perpendicular to each other.)

Hence, (a) Molecule is non-planar. (b) Doesn't show geometrical isomerism because two H at one terminal are equidistant from any H on other terminal. (c) Polar.

Example - 49

Order these species according to increasing C—F bond length : CF^+, CF, CF^-. Predict if any is paramagnetic.

Sol. The molecular orbital electronic configuration of CF (15e) is

$$\sigma ls^2 \sigma^* ls^2 \ \sigma 2s^2 \ \sigma^* 2s^2 \ \sigma 2p_x^2 \ \begin{vmatrix} \pi 2p_y^2 \\ \pi 2p_z^2 \end{vmatrix} \begin{vmatrix} \pi^* 2p_y^1 \\ \pi^* 2p_z^0 \end{vmatrix} \sigma^* 2p_x^0$$

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

In CF^+, there is one 'e' less in antibonding MO, therefore, bond-order = 3, while in CF^-, there is one more 'e' in antibonding MO giving band-order = 2. Since 'Bond-order' is directly related to bond-energy, which is inversely proportional to bond-length, the order of bond-lengths in given series is :

$$CF^+ < CF < CF^-$$

Also, CF and CF^- are paramagnetic because of presence of one and two unpaired electrons respectively, while CF^+ has no unpaired electron and diamagnetic.

Example - 50

Both 'H' and 'F' are monovalent in covalent bonding, phosphorus forms PF_5 but no PH_5 exists. Explain.

Sol. Phosphorus has five electrons in the valence shell ($3s^2 3p^3$) as well as it contains vacant 3d 3d orbitals, so there is scope for pentavalency. However, the 3d orbital of phosphorus is much larger is size than its 3s and 3p-orbitals, and do not usually hybridize. When highly electronegative atoms like F approach to P, its 3d-orbitals, and do not usually hybridize. When highly electronegative atoms like F approach to P, its 3d-orbitals hybridize with 3s and 3p orbitals and enable P to undergo sp^3d hybridization to form PF_5, PCl_5 etc. Hydrogen being very less electronegative, cannot contract 3d orbitals of phosphorus to the level where it can participate in hybridization with 3s and 3p orbitals. Hence, with hydrogen, only s and p orbitals of P hybridize and no more than its three electrons can take part in sharing, showing trivalency only.

Example - 51

Trimethyl amine is a stronger base than trisilyl amine. Explain.

Sol. In trisilyl amine, a $p\pi$-$d\pi$ back bonding occurs as
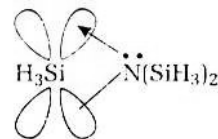
The above $p\pi$-$d\pi$ bond decreases the availability of 1p at nitrogen, thus the basic strength. No such $p\pi$-$d\pi$ bonding is possible in trimethyl amine, hence stronger base.