

Chemical Bonding and molecular structure.

- A group of atoms existing together as one species and having characteristic properties is called molecule.
- The force which holds the atoms together within a molecule is called a chemical bond.
- The atoms of different elements combine with each other in order to complete their respective octates (8 electrons in their outermost shell) or duplet (outermost shell having 2 electron in case of H, Li, Be) to attain stable nearest nobel gas configuration.
- Modes of chemical combination:
 1. By complete transfer of one or more electrons from one atom to another. This process is referred to as electrovalency and the chemical bond formed is electrovalent bond or ionic bond.
 2. By sharing of electron. This can occur in two ways.
 - 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.
- G.N Lewis introduced simple symbols to denote the valance 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.

The Common valancy of the element is either equal to the number of dots (≤ 4) or 8 minus the number of dot (> 4)

- Explanation of the formation of ionic bond:- Atoms are electrically neutral. therefore they possess equal no. of protons and electrons. on losing an electron, an atom become positively charged $A \longrightarrow A^+ + e^-$

On the other hand, in case of atom gaining the electron, the no. of electron exceeds the number of protons and thus the atom become negatively charged $B + e^- \rightarrow B^-$

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

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

The electrostatic field of an ion is non-directional. Each positive ion attracts several negative ion around it depending upon its size or radius, resulting into a three dimensional solid called an ionic crystal.

- The formation of ionic bond depends upon the following factors.
 1. Ionisation enthalpy:- It is the amount of energy required to remove an electron from the outer most shell of an isolated atom in gaseous state so as to convert it into a gaseous positive ion.
 2. Electron gain enthalpy - It is the enthalpy change that take place when an extra electron is added to an isolated atom in the gaseous state to form a gaseous negative ion.
 3. Lattice enthalpy:- The energy released when the requisite number of gaseous positive and negative ions combine to form one mole of ionic compound is called lattice enthalpy. The higher the value of lattice enthalpy, the greater will be the stability of the compound.
The value of the lattice enthalpy depends upon two factors.

- (a) Charge on ions :- The higher the charge on the ions, greater is the force of attraction and hence larger is the amount of energy released.
- (b) Size of the ions :- If the size of the ions is large, internuclear distance will be more and force of attraction will be less while in case of small ions, internuclear distance is less and so force of attraction is greater.
- If Lattice enthalpy + Electron gain enthalpy > Ionization enthalpy the net effect will be the release of energy and hence ionic bond is formed.

General characteristics of Ionic Compound.

1. Physical State - These Compounds usually exist in the solid state.
2. Crystal Structure :- The ionic Compound exist as ion not as molecules. These ions are arranged in a regular pattern in the three dimensional space to form a lattice.
3. High melting and boiling Point - Ionic Compound have high melting and boiling Point, This is because ions are tightly held together by strong electrostatic force of attraction and hence a huge amount of energy required to break the crystal lattice.
4. Solubility :- These 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 crystal and further the high dielectric Constant of the solvent cut off the force of attraction between these ions. the ions may combine with the solvent to liberate energy called the hydration energy which is sufficient to overcome the attractive force between ions.
5. Electrical Conductivity :- these Compounds are good conductor of electricity in solution or in molten state.

6 Ionic reaction - The reactions of the ionic compounds are the reactions between the ions produced in solution. As the opposite charged ions combine quickly, these reactions are quite fast.

- Inert pair effect :- In case of heavier p-block elements like Sn and Pb with the valance shell configuration ns^2np^2 all the four electron may be lost giving a valency +4 or only p-electrons may be lost giving a valency of +2. The s-electrons remain attracted by the nucleus due to the poor screening effect of the intervening d and f electrons and do not take part in bonding. The effect is called inert pair effect.

Note - For the formation of ionic bond between two atoms the electronegativity difference between them should be ≥ 1.9

- 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.

Covalent bond may also be formed by the contribution of two or three electrons by each of two atoms. The bond then formed is called double or triple bond and represent by double ($=$) and triple line ($\equiv$)

- Bond pair - The shared pairs of electrons present between the atoms are called bond pairs because they are responsible for the bonding between the atoms.

- Lone pair - The valance electron not-involved in bonding are called non-bonding or lone pairs or unshared pairs.

— Formal charge on an atom in a molecule/ion:—

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

$$\text{Formal charge} = \text{Total number of valance electron} - \text{Total no of lone pair electrons} - \frac{1}{2} \text{ total no. of shared electrons.}$$

— Significance of formal charge: The main advantage of the calculation of formal charge is that it helps to select the most stable structure. The most stable is the one which has the smallest formal charges on the atoms.

— Limitations of the octet Rule.

(1) Formation of Compounds involving hydrogen: Hydrogen need to complete its duplet and not octet.

(2) Formation of Compounds like BeCl_2 , BF_3 , AlCl_3 ...

In each of these molecules the central atom has less than 8 electrons, these are electron deficient compounds.

(3) Formation of Compounds like PCl_5 , SF_6 , IF_7 , H_2SO_4 :-

In each of these molecules the central atom has more than 8 electrons. These compounds are called hypervalent compounds.

(4) Formation of Compounds of noble gases: Noble gases which have already complete octets should not form compounds. However their compounds have been prepared like XeF_2 , XeF_4 , XeF_6 , KrF_2 etc.

(5) Odd electron bond/odd electron molecules :- There are some molecules and ions in which the bonded atoms contain odd.

number of electrons between them. The bond thus present are called odd electron bond and the molecules are called odd electron molecules.

— Limitations of Lewis - Langmuir Concept of Covalent bond.

- (i) It could not explain how the atoms are held together in the molecules
- (ii) It could not explain the shape of molecules containing Covalent bond.
- (iii) It could not explain the release of energy during the formation of a Covalent bond.

— Valence Shell electron pair repulsion theory. (VSEPR):
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.

Basic assumption.

1 The shape of a molecule containing only two atoms is always linear.

- (i) For molecules containing 3 or more atoms, one of the atoms is called the central atom to which other atoms are linked.
- (ii) If the central atom is linked to similar atoms and is surrounded by bond pairs of electrons only, the repulsions between them are similar. As a result the shape of the molecule is symmetrical and molecule is said to have a regular geometry.
- (iv) If the central atom is linked to different atoms or is surrounded by bond pair as well as lone pairs of electrons.

The repulsions between them are different. As a result the molecule has an irregular or distorted geometry. the order of repulsion.

Lone Pair - Lone Pair > Lone Pair - Bond Pair > Bond Pair - Bond Pair.

(v) The exact shape of the molecule depends upon the total number of electron pairs present around the central atom.

— Calculation of total number of electron pairs, bond pairs and lone pairs and predicting the shape of the molecules and ions.

(i) Total number of electron pair around the central atom.

$$= \frac{1}{2} (\text{No. of valance electron of central atom} + \text{no. of atoms linked to the central atom by single bond})$$

— For Negative ion, add number of electron equal to the units of negative charge on the ion.

— For positive ion, subtract number of electrons equal to the units of positive charge on the ion.

(ii) No. of Bond Pair = No. of atoms linked to central atom by single bond and it is represent by (B)

(iii) No. of lone pair = Total no. of electron pair - No. of shared pair.

and it is represented by (L)
 table for shape.

AB_2Lo — Linear — 180°

AB_3Lo — Trigonal planar — 120°

AB_2L — Bent (V shape) — two angle more than 120° .
 and one angle less than 120°

AB_4Lo — Tetra hedral — $109^\circ 28''$

AB_3L — Trigonal Pyramidal — less than $109^\circ 28''$

AB_2L_2 — Bent (V shape) — " "

AB_5Lo — Trigonal bi Pyramidal — 3 (120°) 2 (90°)

AB_4L — See Saw. — 2 (90°)

AB_3L_2 — T Shaped

AB_2L_3 — Linear.

AB_6 — Octahedral.

AB_5L — Square Pyramidal

AB_4L_2 — Square Planar.

— Valence bond theory of Covalent bond (a) In term of energy.

(i) The forces of repulsion between the nuclei of combining atoms and between the electrons of these atoms. these forces tend to increase the energy of the system.

(ii) The forces of attraction between the nucleus of one atom and electrons of the other atom, the force tends to decrease the energy of the system.

The energy required to break one mole of bonds of the same kind is known as bond energy or bond dissociation energy.

(b) In term of orbital overlap Concept :- A Covalent bond is formed by the partial overlap of two half filled atomic orbitals containing electrons with opposite spins.

— Types of Covalent Bond.

1. Sigma bond (σ) :- 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 bond. and it is represented by (σ). It is a strong bond.

2. Pi (π) Bond :- Pi bond is formed by lateral (sideway) overlapping of p-orbital by overlapping of p-orbitals in a direction at right angles to the internuclear axis. It is a weak bond.

Difference between Sigma and Pi bond.

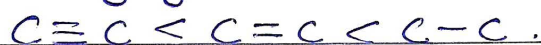
σ Bond.	π bond.
(1) This bond is formed by overlap of orbital along their internuclear axis.	This is formed by sideways overlapping of orbitals.
(2) This is formed by overlapping between S-S, S-P and P-P orbitals.	This is formed by overlap of P-P orbitals only.
(3) It is a strong bond.	It is a weak bond.
(4) Electron cloud is symmetrical about the line joining the two nuclei.	Electron cloud in π bond is not symmetrical.
(5) Sigma bond consists of only one electron cloud symmetrical about the internuclear axis.	π bond consists of two clouds one above and other below the plane of atomic nuclei.
(6) Free rotation about a σ bond is possible.	Free rotation about a π bond is not possible.

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

factor affecting bond length.

1. Size of the atom — It increases with increase in size of atom so $HI > HBr > HCl > HF$.

2. Multiplicity of bond — The bond length decreases with the multiplicity of the bond so



3. Type of hybridization — $sp^3 > sp^2 > sp$.

— Bond enthalpy — 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 bond enthalpy.

factor affecting bond enthalpy.

- (i) Size of the atoms :- Greater the size of the atom greater is the bond length and less is the bond dissociation enthalpy. less is the bond strength.
- (ii) multiplicity of bonds :- Greater is the multiplicity of the bond, greater is the bond dissociation enthalpy.



- (iii) Number of lone Pairs of electron Present :- Greater the no. of lone pair of electron present, greater is the repulsion between the atoms and hence less is the bond dissociation energy.

— Bond angle :- The angle between the line representing the direction of the bonds, the orbitals containing the bonding electrons is called the bond angle.

— Bond order — In the Lewis representation of a molecule or ion, the number of bonds present between two atoms is called bond order.

- (a) Greater the bond order, greater is the stability of the bond and greater is bond enthalpy.
- (b) Greater the bond order shorter is the bond length.

— Non Polar Covalent bond :- If two similar atoms come close to each other and form a bond by sharing their electrons, the shared electrons are equally attracted by the two atoms as the electronegativity of the atoms is same. So the shared electrons are not displaced. Hence no poles are developed.

— Polar Covalent bond :- When two dissimilar atoms having different electronegativity combine together to form a covalent bond, the shared pair of electron

does not lie at equal distance from the nuclei of both the bonded atom but shift towards the atom having greater electronegativity as a result one end of the molecule having more electronegativity atom becomes slightly negative charged while the other end acquired slightly positive charged thus the negative and positive poles are developed and this type of bond is called Polar Covalent bond.

— Partial ionic character of Covalent bond.

(a) If the electronegativity difference between two atoms is 1.9, the bond is said to have 50% Ionic character and 50% Covalent character.

(b) If the electronegativity difference between the atoms is more than 1.9, then the partial ionic character of the bond is more than 50% and bond is taken as ionic.

(c) If the electronegativity difference between two atoms is less than 1.9, the bond is predominantly covalent.

— Pauling equation:

$$\text{Ionic Character } \% = 16 (X_A - X_B)^{1.4}$$

— Hannay and Smith equation:-

$$\text{Ionic Character } \% = 16 (X_A - X_B) + 3.5 (X_A - X_B)^2$$

— Dipole moment:- The product of magnitude of negative or positive charge (q) and the distance (d) between the centers of positive and negative charge is called dipole moment. It is denoted by μ

$$\mu = q \times d$$

(a) Dipole moment in diatomic molecules:- As a polar diatomic molecule possesses only one polar bond, the dipole moment of that molecule is equal to the dipole moment of the polar bond. Greater the electronegativity difference between the bonded atoms, greater is the dipole moment.

(b) Polyatomic molecules:- As a Polyatomic molecule has more than one polar bond, the dipole moment is equal to the resultant dipole moment of all the individual bond. The magnitude of this resultant dipole moment not only depend upon the values of the individual dipole moment of the bonds but also on their arrangement in space.

example.

— Comparison of dipole moment of NH_3 and NF_3 —

Both NH_3 and NF_3 molecules have pyramidal shapes with one lone pair of electrons on N atom. As F is highly electronegative, so N-F bond should be more polar and net dipole moment of NF_3 should be much greater than that of NH_3 . But NF_3 has much lesser dipole moment than NH_3 because.

(i) The dipole formed between the lone pair and N atom has to be taken in consideration which is in the direction of lone pair.

(ii) F is more electronegative than N, therefore direction of bond is from N to F whereas N is more electronegative than H therefore direction of bond is from H to N.

thus resultant moment of N-H bond adds up to the bond moment of lone pair, that of 3 N-F bond partly cancels the resultant moment of lone pair, hence the net-dipole moment of NF_3 is less than NH_3 .

— Applications of dipole moments.

(a) In determining the Polarity of bonds:- As $\mu = q \times d$, greater is the magnitude of dipole moment higher will be the Polarity of the bond. This concept is applicable to molecules containing only one-polar bond.

(b) In the Calculation of Percentage Ionic character.

$$\mu_{\text{ionic}} = q \times d.$$

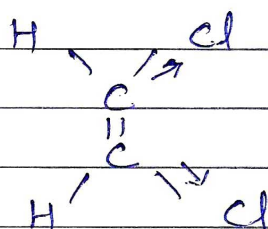
$$\% \text{ ionic char.} = \frac{\mu_{\text{observed}}}{\mu_{\text{ionic}}} \times 100.$$

$$\left[\begin{array}{l} d - \text{bond length.} \\ q - \text{Charge } (4.8 \times 10^{-10} \text{ esu}) \end{array} \right]$$

(c) In determining the Symmetry or Shape of the molecules:-

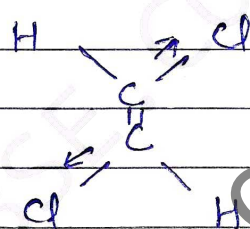
(d) To distinguish between cis and trans isomers-

This is based on the fact that cis isomer usually has higher dipole moment than trans isomer. This is because in the trans isomer, the bond moments of C-Cl Cancel each other.



cis

$[\mu \neq 0]$

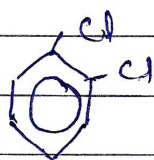


trans

$[\mu = 0]$

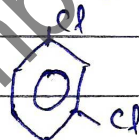
(e) To distinguish between Ortho, meta and Para isomers.

This is based on the fact that the dipole moment of Para isomer that of ortho is greater than meta.



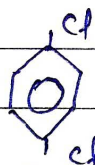
Ortho

$\mu = 2.54D$



meta

$\mu = 1.48D$



Para

$\mu = 0$

— Partial Covalent Character of ionic bonds (Fajan's Rule)

When a Cation approaches an anion, the electron cloud of the anion is attracted towards the Cation and hence get distorted. The Power of the Cation to Polarise the anion is called its Polarising Power and the tendency of the anion to get Polarised is called its Polarizability.

The greater is the Polarisation produced, more is the neutralisation of the Charge and hence the ionic character is decreases and Covalent Character increases.

The formation of Covalent bond is favoured by the following factors.

- (a) **Small Size of the Cation:** - Smaller the Cation, greater is its Polarising Power. $\text{LiCl} > \text{KCl}$.
- (b) **Large Size of anion:** - Larger the anion, greater is its Polarizability. $\text{LiI} > \text{LiBr} > \text{LiCl} > \text{LiF}$.
- (c) **Large Charge on the Cation or anion:** - Larger the charge on the Cation, greater is its Polarising Power. Hence Covalent character increases.
 $\text{Al}^{+3}\text{Cl}_3 > \text{Mg}^{+2}\text{Cl}_2 > \text{Na}^+\text{Cl}$
- (d) **Electronic Configuration of the Cation:** If the two Cation have the same size and charge then the one with noble gas Configuration with 18 electrons in outermost shell has greater Polarising Power than the other with noble gas Configuration with 8 electrons in the outermost shell.
 $\text{CuCl} > \text{NaCl}$.

- Characteristics of Covalent bond.

- (a) **Physical State:** - Covalent Compounds exist in all the three states.
- (b) **Crystal Structure:** - they usually consist of molecules rather than ions.
- (c) **Melting and boiling Point:** - they have low melting and boiling point.
- (d) **Solubility:** - Covalent Compounds are generally soluble in organic solvent but insoluble in water and other polar solvent.
- (e) **Electrical Conductivity** - they are bad conductors of electricity.
- (f) **Non-Ionic reactions** - their reactions are molecular and proceed at a much slower rate than those of ionic compounds.
- (g) **Directional Characteristics and Isomerism** - Atom in a molecule can take up different directional arrangement.

and thus show structural and stereo-isomerism.

— Hybridisation — It is defined as the mixing of the atomic orbital 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.

— Important Points about Hybridisation.

1. Only those orbitals which have approx. equal energies and belong to the same atom or ion can undergo hybridisation.
2. Number of hybrid orbitals produced is equal to the number of atomic orbitals mixed.
3. It is not necessary that all the half filled orbitals must participate. Even completely filled orbitals with slightly different energies can also participate.
4. Hybridisation never takes place in isolated atoms but it occurs only at the time of bond formation.
5. Type of hybridisation indicates the geometry of molecules.
6. The bigger lobe of the hybrid orbital always has positive sign while the smaller lobe on the opposite side has negative sign.

— Types of hybridisation

- (a) 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.

They are collinear with an angle of 180° . Each of the hybrid orbitals formed has 50% s -character and 50% p character.

(b) 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.

All the three hybrid orbitals remain in the same plane making an angle of 120° .

Each of the hybrid orbitals formed has $\frac{1}{3}$ (s) character and $\frac{2}{3}$ (p) character.

(c) Tetrahedral or sp^3 hybridisation :- When one s and three p-orbitals belonging to the same shell of an atom mix together to form four new equivalent orbitals, the type of hybridisation is called sp^3 or tetrahedral hybridisation. The new orbitals are called sp^3 or tetrahedral orbitals.

These are directed towards the four corners of a regular tetrahedron and make an angle of $109^\circ 28'$.

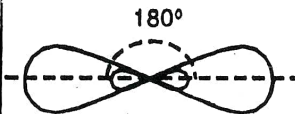
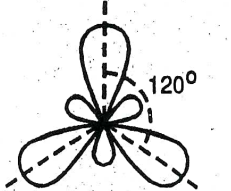
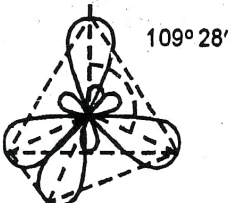
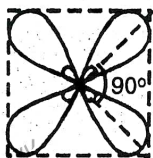
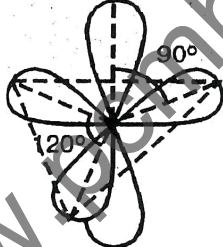
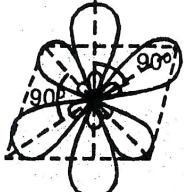
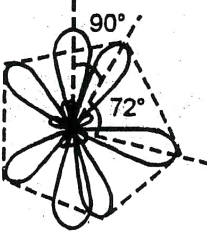
Each sp^3 hybrid orbital has 25% s-character and 75% p-character.

— Geometry or Shape of the molecule :- A particular arrangement obtained by bonding a number of atoms in definite directions to the central atom of a molecule is called the geometry or shape of the molecules.

Conclusion:

(i) In similar molecules as the electronegativity of the central atom decreases and the size increases the bond angle decreases.

(ii) In similar molecules, as the electronegativity of the surrounding atoms decreases the bond angle increases.

Types of Hybridisation	Atomic orbitals involved	Representing directions of hybrid orbitals formed alongwith bond angles	Shape of the molecule	Examples
1. sp	one s + one p		Linear	BeCl_2 , BeH_2 , C_2H_2 , HgCl_2
2. sp^2	one s + two p		Triangular planar	BF_3 , BCl_3 , C_2H_4 , NO_3^- , CO_3^{2-}
3. sp^3	one s + three p		Tetrahedral	CH_4 , CCl_4 , SnCl_4 , NH_4^+
4. dsp^2	one d ($d_{x^2-y^2}$) + one s + two p		Square planar	$[\text{Ni}(\text{CN})_4]^{2-}$, $[\text{PtCl}_4]^{2-}$
5. sp^3d	one s + three p + one d (d_{z^2})		Trigonal bipyramidal	PF_5 , PCl_5
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 , $[\text{CrF}_6]^{3-}$, $[\text{Co}(\text{NH}_3)_6]^{3+}$
7. sp^3d^3	one s + three p + d_{xy} , d_{yz} , d_{xz}		Pentagonal bipyramidal	IF_7

PREDICTING HYBRIDISATION OF CENTRAL ATOM AND SHAPES OF SIMPLE MOLECULES/IONS

(a) **Predicting hybridisation.** Calculate the number of hybrid orbitals (X) to be formed by the central atom as follows :

$$X = \frac{1}{2} \left[\left\{ \begin{array}{l} \text{No. of valence electrons} \\ \text{of the central atom} \end{array} \right\} + \left\{ \begin{array}{l} \text{No. of monovalent atoms/groups} \\ \text{surrounding the central atom} \end{array} \right\} - \left\{ \begin{array}{l} \text{Charge on the cation} \\ \text{if the given species is} \\ \text{a polyatomic cation} \end{array} \right\} + \left\{ \begin{array}{l} \text{Charge on the anion} \\ \text{if the given species} \\ \text{is a polyatomic anion} \end{array} \right\} \right]$$

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

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

(b) **Predicting shape.** If number of hybrid orbitals is equal to the number of surrounding atoms/groups (monovalent or divalent etc.) the molecule/ion has a regular geometry and the shape is same as that predicted by hybridisation. However, if number of surrounding atoms/groups is less than the number of hybrid orbitals, the difference gives the number of lone pairs present on the central atom and the species is said to have irregular geometry and the shape is predicted by leaving the hybrid orbitals containing the lone pairs.

Note that in predicting the shape, only number of atoms or groups are to be considered irrespective of the fact that they are monovalent or divalent etc.

A few examples to predict the hybridisation of the central atom and shape of the molecule/ion are given below :

	Molecule/Ion	$X = \frac{1}{2} [VE + MA - c + a]$	Hybridisation	Hybrid orbitals containing lone pairs	Shape
(i)	CO_2 (${}_6C = 2, 4$)	$X = \frac{1}{2} [4 + 0 - 0 + 0] = 2$ (MA = 0 as oxygen is divalent) $c = 0, a = 0$, as it is neutral molecule)	sp	0	Linear
(ii)	BF_3 (${}_5B = 2, 3$)	$X = \frac{1}{2} [3 + 3 - 0 + 0] = 3$ (MA = 3 as three F's are monovalent)	sp^2	0	Planar triangular
(iii)	SiF_4 (${}_{14}Si = 2, 8, 4$)	$X = \frac{1}{2} [4 + 4 - 0 + 0] = 4$	sp^3	0	Tetrahedral
(iv)	PCl_5 (${}_{15}P = 2, 8, 5$)	$X = \frac{1}{2} [5 + 5 - 0 + 0] = 5$	sp^3d	0	Trigonal bipyramidal
(v)	SF_6 (${}_{16}S = 2, 8, 6$)	$X = \frac{1}{2} [6 + 6 - 0 + 0] = 6$	sp^3d^2	0	Octahedral
(vi)	NH_3 (${}_7N = 2, 5$)	$X = \frac{1}{2} [5 + 3 - 0 + 0] = 4$ (MA = 3 as three H's are monovalent)	sp^3	1	Pyramidal
(vii)	PCl_3 (${}_{15}P = 2, 8, 5$)	$X = \frac{1}{2} [5 + 3 - 0 + 0] = 4$ (MA = 3 as three Cl's are monovalent)	sp^3	1	Pyramidal

	Molecule/Ion	$X = \frac{1}{2} [VE + MA - c + a]$	Hybridisation	Hybrid orbitals containing lone pairs	Shape
(viii)	IF ₅	$X = \frac{1}{2} [7 + 5 - 0 + 0] = 6$	$sp^3 d^2$	1	Square pyramidal
(ix)	IF ₇	$X = \frac{1}{2} [7 + 7 - 0 + 0] = 7$	$sp^3 d^3$	0	Pentagonal bipyramidal
(x)	H ₂ O (₈ O = 2, 6)	$X = \frac{1}{2} [6 + 2 - 0 + 0] = 4$	sp^3	2	Bent (V-shaped)
(xi)	NH ₄ ⁺ (₇ N = 2, 5)	$X = \frac{1}{2} [5 + 4 - 1 + 0] = 4$ ($c = 1$ as charge on cation = 1)	sp^3	0	Tetrahedral
(xii)	H ₃ O ⁺ (₈ O = 2, 6)	$X = \frac{1}{2} [6 + 3 - 1 + 0] = 4$	sp^3	1	Pyramidal
(xiii)	CH ₃ ⁺ (Carbocation)	$X = \frac{1}{2} [4 + 3 - 1 + 0] = 3$	sp^2	0	Triangular planar
(xiv)	NO ₃ ⁻ (₇ N = 2, 5)	$X = \frac{1}{2} [5 + 0 - 0 + 1] = 3$ ($a = 1$ as charge on anion = 1)	sp^2	0	Triangular planar
(xv)	CO ₃ ²⁻ (₆ C = 2, 4)	$X = \frac{1}{2} [4 + 0 - 0 + 2] = 3$ ($a = 2$ as charge on anion = 2)	sp^2	0	Triangular planar
(xvi)	SO ₄ ²⁻ (₁₆ S = 2, 8, 6)	$X = \frac{1}{2} [6 + 0 - 0 + 2] = 4$ ($MA = 0$ as oxygen is divalent)	sp^3	0	Tetrahedral
(xvii)	ClO ₄ ⁻ (Perchlorate ion)	$X = \frac{1}{2} [7 + 0 - 0 + 1] = 4$	sp^3	0	Tetrahedral
(xviii)	CH ₃ ⁻ (Carbanion)	$X = \frac{1}{2} [4 + 3 - 0 + 1] = 4$	sp^3	1	Pyramidal

— Resonance — In case of certain molecules, a single Lewis structure cannot explain all the properties of the molecule. The molecule is then supposed to have many structures each of which can explain all the properties of the molecule but none can explain all the properties of the molecule. The actual structure is in between of all these contributing structures and is called resonance hybrid and the different individual structures are called resonating structures or canonical forms. This phenomenon is called resonance.

Rules for writing the resonating structures.

- (i) The contributing structures should have the same position of atoms, they should differ only in the position of electrons.
- (ii) The contributing structures should have the same number of unpaired electrons.
- (iii) The contributing structures should have nearly same energy.
- (iv) The contributing structures should have negative charge on the electronegative atom and positive charge on the electropositive atom.
- (v) In the contributing structures, like charges should not be present on adjacent atom while unlike charges should not be widely separated.

— Resonance energy — The difference in the energy of the resonance hybrid and the most stable contributing structure having least energy is called resonance energy.

— Characteristics of Resonance —

- (a) The contributing structures do not have any real existence. They are only imaginary. Only the resonance hybrid has the real existence.
- (b) As a result of resonance, the bond lengths in a molecule become equal.

- (c) The resonance hybrid has lower energy, greater is the stability.
- (d) Greater is the resonance energy, greater is the stability of the molecule.
- (e) Greater is the number of Canonical forms with nearly same energy, greater is the stability of the molecule.

— Molecular orbital theory.

The main ideas of this theory may be.

- (1) When two atomic orbitals combine or overlap, they lose their identity and form new orbitals. The new orbitals are called molecular orbitals.
- (2) Molecular orbitals are the energy states of a molecule in which the electrons of the molecule are filled just as atomic orbitals are the energy states of an atom in which the electrons of the atom are filled.
- (3) A molecular orbital gives the electron probability distribution around a group of nuclei.
- (4) Only those atomic orbitals can combine to form molecular orbitals which have comparable energies and proper orientation.
- (5) The number of molecular orbitals formed equal to the number of combining atomic orbitals.
- (6) When two atomic orbitals combine, they form two new orbitals called bonding molecular orbital and antibonding molecular orbital.
- (7) The bonding molecular orbital has lower energy and hence greater stability than the corresponding antibonding molecular orbitals.
- (8) The bonding molecular orbitals are represented by (σ) and (π) whereas antibonding molecular orbitals are represented by (σ^*) and (π^*) .

(9) The shapes of the molecular orbitals formed depend upon the type of the combining atomic orbitals.

(10) The filling of molecular orbitals take place according to the same rules as those of the atomic orbitals.

— Bonding molecular orbital — The molecular orbital formed by the additive effect of the atomic orbitals is called bonding molecular orbital.

— Antibonding molecular orbital — The molecular orbital formed by the subtractive effect of the atomic orbitals is called antibonding molecular orbital.

— Stabilization energy : — The lowering of energy of the bonding molecular orbital than the combining atomic orbital is called stabilization energy.

— Destabilization energy : — Increase in energy of the antibonding molecular orbital than the combining atomic orbital is called destabilization energy.

— Characteristics of Bonding molecular orbitals.

(a) The probability of finding the electron in the inter nuclear region is greater than that of the combining atomic orbitals.

(b) The electrons present in the bonding molecular orbital result in an attraction between the two atoms.

(c) As a result of attraction, the bonding molecular orbital has lower energy and hence greater stability.

(d) They are formed by the additive effect of the atomic orbitals.

(e) They are represented by (σ) and (π)

— Characteristics of antibonding molecular orbitals.

- (a) The probability of finding the electron in internuclear region decreases
- (b) The electron present in the anti bonding molecular orbital, result in the repulsion between the two atoms.
- (c) Because of repulsive force, anti bonding molecular orbitals has higher energies and lower stability.
- (d) They are formed by the subtractive effect of the atomic orbitals
- (e) They are represented by (σ^*) and (π^*)

— Condition for the combination of atomic orbitals to form molecular orbitals.

1. The Combining atomic orbitals should have comparable energies.
2. The Combining atomic orbitals must have proper orientations so that they are able to overlap to a considerable extent.
3. The extent of overlapping should be large, greater will be the electron density between the nuclei.

— Relation between electronic configuration and molecule

1. Stability of molecules in terms of bonding and anti-bonding electrons:-

Let the no. of electrons present in the bonding orbitals is represented by N_b and the number of electrons present in the antibonding orbital by N_a .

- (a) If $N_b > N_a$ the molecule is stable. (Net attraction)
- (b) If $N_b < N_a$ the molecule is unstable (Net repulsion)
- (c) If $N_b = N_a$ The molecule is unstable.

2. Stability of molecule in term of Bond order:-

Bond order is defined as half of the difference between the number of electrons present in the bonding and the anti

bonding orbitals.

$$\text{Bond order} = \frac{1}{2} (N_b - N_a)$$

If bond order is Positive the molecule is stable and if the bond order is negative or zero then the molecule is unstable.

3. Relative stability of molecule in term of bond order :-
For diatomic molecules the stability is directly proportional to the bond order.

Stability $\propto$ Bond order.

4. Nature of bond in term of bond order :- Bond order 1, 2, 3 means single, double and triple bond. The difference between a chemical bond and bond order lies in the fact that a chemical bond is always integral but bond order can be fractional also.

5. Bond length :- $\text{Bond length} \propto \frac{1}{\text{Bond order}}$

Greater the bond order, shorter the bond length.

6. Diamagnetic and Paramagnetic nature :- If all the electrons in the molecule are paired, it is diamagnetic in nature and if the molecule has some unpaired electrons it is Paramagnetic.

Difference.

Valence Bond.	Molecular Bond.
1. The atomic orbitals of the combining atom retain a large amount of their individual character.	Atomic orbitals of the combining atoms lose their individual identity.
2. Resonance play an important role.	Resonance has no role.
3. It fails to explain Paramagnetism of O_2 .	It explains easily the Paramagnetism of O_2 .

- | | |
|---|---|
| 4. Mathematically, it is simple to apply. | It is difficult to apply. |
| 5. It fails to explain the possibility and existence of H_2^+ | It explain the possibility and existence of H_2^+ . |

— Calculation of Bond order for molecules showing resonance—

$$\text{Bond order} = \frac{\text{Total no. of bond between two atoms in all structure}}{\text{Total no. of resonating structure}}$$

— Hydrogen Bonding :- Whenever a molecule contains a hydrogen atom linked to a highly electronegative atom, this atom attracts the shared pair of electrons more and so this end of the molecule become slightly negative while the other end is slightly positive. The negative end of one molecule attracts the positive end of the other and as a result, a weak bond is formed between them. This bond is called hydrogen bond.

As a result of hydrogen bonding, a H-atom links the two electronegative atom, one by covalent bond and other by a hydrogen bond, hence it is said to form a hydrogen bridge.

— Condition for hydrogen bonding.

1. The molecule must contain a highly electronegative atom linked to H-atom
2. The size of the electronegative atom should be small, so only F, O, N atoms can form hydrogen bond.

— Effects of hydrogen bond.

- (a) Dissociation :- In aqueous solution hydrogen fluoride dissociate and give the difluoride ion instead of fluoride ion. This explain:

the existence of KHF_2 and non existence of KHD_2 , CH_3BO_2 and KHI_2 .

- (b) **Association** - The molecules of Carboxylic acids exist as dimers because of hydrogen bonding. The molecular mass of such compounds are found to be double than those calculated from their sample.
- (c) **High melting and boiling point** - The high melting points and boiling points of the compounds containing hydrogen bond is due to the fact that some extra energy is needed to break these bonds.
- (d) **Solubility** :- The compounds which can form hydrogen bonds with the solvent molecules are soluble in such solvents.
- (e) **Volatility** :- As the compounds involving hydrogen bonding between different molecules have higher boiling points so they are less volatile.
- (f) **Viscosity and surface tension** - The substance which contain hydrogen bond have higher viscosity and high surface tension.

Types of hydrogen bonding.

- (1) **Intermolecular bond** - When hydrogen bond take place between different molecules of the same or different compound is called intermolecular hydrogen bond.
- (2) **Intramolecular bond** - When the hydrogen bond take place within a molecule itself is called intramolecular hydrogen bond.

- **Significance of hydrogen bonding in biological system** :- Water present in plants and animals which is more than 50% by weight is attached to the proteins by hydrogen bonding. The structure of proteins and nuclei acids are stabilized by hydrogen bonding.

Difference

Hydrogen bond	Covalent bond
(1) It involve dipole-dipole attractive interaction.	It involves sharing of electrons.
(2) It is formed between H and a high electronegative atom.	It is formed between two electronegative atoms.
(3) The strength of this bond is very small.	The bond strength of this bond is sufficiently high.
Atomic orbital	molecular orbital
(1) Their electron cloud extends around the nucleus of a single atom. atomic orbital is monocentric	The electron cloud extends around all the nuclei of bonded atom. molecular orbital is polycentric
2. They are less stable	They are more stable.
3. They have simple shape	they have complex shape.
molecular Sigma bond	molecular- π -bond
(1) The bond is formed by overlap of orbitals along their internuclear axis.	This is formed by sideways overlapping of orbitals (lateral)
(2) This is formed by s-s, s-p or p-p.	This is formed by overlap of p-p
(3) It is a strong bond	It is a weak bond.
(4) Electron cloud in this case is symmetrical about the line joining the two nuclei	Electron cloud is not symmetrical
(5) Sigma bond consist of only one electron cloud symmetrical about the internuclear axis.	π -bond consists of two electron clouds, one above the plane of atomic nuclei and other below it.
(6) Free rotation about a (σ) bond is possible.	Free rotation is not possible because on rotation, overlapping vanishes and the bond is break.