

CHEMICAL BONDING AND MOLECULAR STRUCTURE

The attractive force that binds the atoms together in a molecule is called a chemical bond. It is formed either by the transfer of electrons or by the sharing of electrons.

Lewis symbols

In the formation of a chemical bond, only the outermost electrons participate and these electrons are called valence electrons. The inner electrons are well protected and they are called core electrons.

G.N Lewis introduced simple notations to represent valence electrons in an atom. These notations are called Lewis symbols or Lewis notations. Here the nucleus and the inner electrons are represented by the symbol of the element and the valence electrons by dots or crosses.

E.g. for sodium [₁₁Na -2,8,1], the Lewis symbol is Na and for chlorine [₁₇Cl -2,8,7], the Lewis symbol is Cl

Lewis symbols are informative. It gives the valency of an atom, which is either equal to the number of dots or crosses or equal to 8 – no. of dots or crosses.

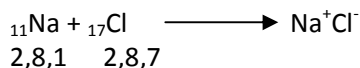
Octet rule

This rule was proposed by Lewis and Kossel. According to this rule, *atoms undergo chemical reaction in order to attain octet of electrons in the valence shell. Or, atoms containing 8 electrons in their valence shell are stable.* To attain octet, they share electrons or exchange electrons.

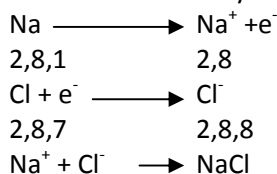
Ionic or Electrovalent Bond

A bond formed by the transfer of electron between 2 atoms is called ionic or electrovalent bond. Or, it is the force of attraction between two oppositely charged ions.

E.g. formation of NaCl



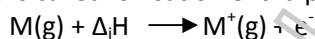
In Na atom, there is only one electron in the valence shell and in Cl, there are 8 electrons in the valence shell. In order to attain octet state, Na atom loses one electron and form Na⁺ ion and Cl atom gains one electron and form Cl⁻ ion. These two ions attract each other by electrostatic force called ionic bond.



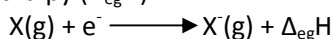
Energy changes during the formation of an ionic bond

An ionic bond formation involves the following steps:

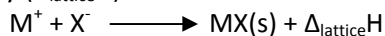
- 1) The formation of a positive ion (cation) from the electropositive atom. The amount of energy required for this process is called ionisation enthalpy ($\Delta_i H$).



- 2) Formation of negative ion from the electronegative atom. The energy involved in this process is called electron gain enthalpy ($\Delta_{eg} H$).



- 3) The packing of the cation and anion to form an ionic compound. The energy change in this process is called lattice enthalpy ($\Delta_{\text{lattice}} H$)



So the factors favouring the ionic bond formation are:

- i) Low ionisation enthalpy of the electropositive atom (metal atom)
- ii) High negative electron gain enthalpy of the electronegative atom (non-metal atom)
- iii) High lattice enthalpy of the ionic compound formed.

Lattice Enthalpy

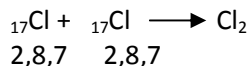
It is the energy required to completely separate one mole of an ionic compound into corresponding gaseous ions. Or, it is the energy liberated when one mole of an ionic compound is formed from gaseous ions.

The stability of an ionic compound is determined by its Lattice Enthalpy. Generally greater the Lattice Enthalpy, stabler will be the compound.

Covalent bond

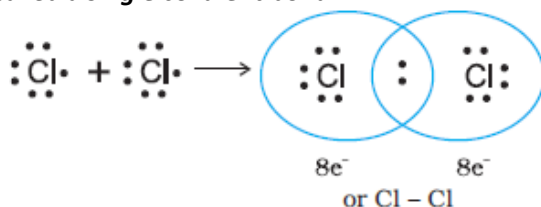
A bond formed by the mutual sharing of electrons between two or more atoms is called covalent bond.

e.g. 1) The formation of Chlorine molecule (Cl_2)

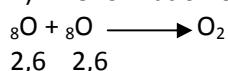


Both the chlorine atoms have 7 electrons in their outermost shell. So here the exchange of electrons is not possible. For the formation of Cl_2 molecule, each Cl atom shares one pair of electron.

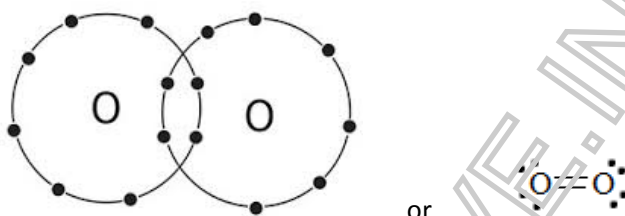
The bond thus formed is called a **single covalent bond**.



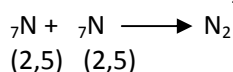
2) The formation of O_2 molecule



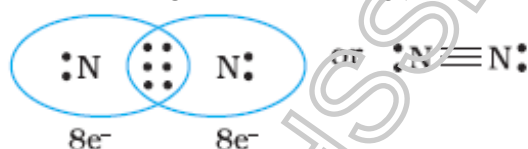
To attain octet, each oxygen atom shares 2 pairs of electrons. Thus a **double covalent bond** is formed.



3) The formation of N_2 molecule



To attain the octet configuration, the nitrogen atoms share 3 pairs of electrons. Thus a **triple bond** is formed.



In the formation of a covalent bond, each combining atoms contribute at least one electron to the shared pair. The number of electrons contributed by an atom to the shared pair (bonded pair) during the formation of a covalent bond is called covalency. In the formation of Cl_2 molecule, the covalency of each Cl atoms is one, in O_2 molecule, the covalency of O atom is 2 and in N_2 , it is 3.

The double and triple bonds are together called **multiple bonds**. A covalent bond formed by the sharing of one pair of electron is called a **single bond**. A double bond is formed when 2 pairs of electrons are shared between 2 atoms and a triple bond is formed when 3 pairs of electrons are shared between two atoms.

Limitations of Octet rule

- 1) It could not explain the stability of compounds containing less than 8 electrons around the central atom. E.g. LiCl , BeH_2 , BCl_3 etc.
- 2) It could not explain the stability of molecules containing odd number of electrons like NO , NO_2 etc.
- 3) It could not explain the stability of molecules containing more than 8 electrons around the central atom (i.e. expanded octet). E.g. PF_5 , SF_6 , H_2SO_4 , IF_7 etc.
- 4) octet rule is based upon the chemical inertness of noble gases. But some noble gases like xenon and krypton form compounds with F and O.
- 5) This theory does not account for the shape of molecules.
- 6) It does not explain the relative stability of the molecules.

Bond Parameters

- 1) **Bond Length:** It is defined as the average equilibrium distance between the nuclei of two bonded atoms in a molecule. It is measured by spectroscopic, X-ray diffraction and electron diffraction techniques. It is expressed in pico-metre (pm) or in angstrom unit (\AA).
- 2) **Bond Angle:** It is defined as the angle between the orbitals containing bonding electron pairs around the central atom in a molecule. It can be experimentally determined by spectroscopic methods. It is expressed in degree.
- 3) **Bond Enthalpy:** It is defined as the amount of energy required to break one mole of a particular bond between 2 atoms in gaseous state. Its unit is kJ/mol.

For diatomic molecules, bond enthalpy is equal to bond dissociation enthalpy. Larger the bond dissociation enthalpy, stronger will be the bond formed. For poly atomic molecules, the bond enthalpy is the average of the bond dissociation enthalpies.

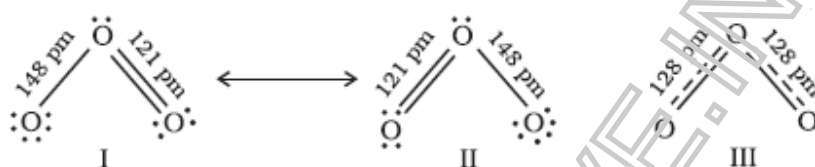
- 4) **Bond order:** It is defined as the number of bonds between 2 atoms in a molecule. For H_2 , bond order = 1, for O_2 , bond order = 2 and for N_2 , bond order = 3. Isoelectronic molecules and ions have identical bond orders.

Generally with increase in bond order, bond enthalpy increases and bond length decreases.

Resonance Structures

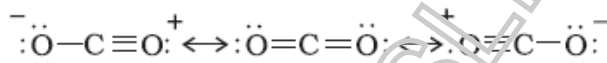
In the case of some compounds, all the observed properties cannot be explained by a single structure. Here we use more than one structures of the compound. These different structures are called *resonance structures or canonical structures or contributing structures*. The phenomenon is known as *resonance*. Resonating structures are separated by double headed arrows.

e.g. i) Ozone (O_3)

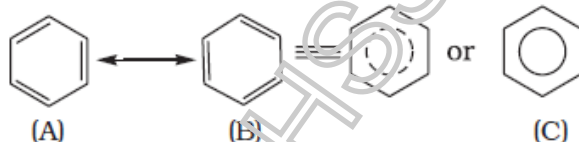


The actual structure of ozone is not I or II. It is a resonance hybrid of the structures I and II which can be represented as structure III.

ii) Carbon dioxide (CO_2)



iii) Benzene (C_6H_6)



Characteristics of resonance

- a) Resonance stabilizes the molecule. As the number of resonating structures increases, the stability also increases.
- b) Resonance changes the bond length.
- c) The difference in energy between the actual structure and the most stable canonical structure is called resonance energy. Greater the resonance energy, stabler will be the molecule.

Polarity of bonds – Dipole moment

When a covalent bond is formed between 2 similar atoms, the shared pair of electrons is equally attracted by the two atoms. So the electron pair is exactly between the two nuclei. The bond so formed is called a non-polar covalent bond.

But when the covalent bond is formed between 2 dissimilar atoms, the shared electron pairs are more attracted by one of the atoms. So one atom gets a slight negative charge (δ^-) and the other gets a slight positive charge (δ^+). Such molecules are called polar molecules. E.g. HCl , HF , H_2O , HI etc.

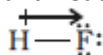
The polarity of a molecule is expressed in terms of *dipole moment* (μ). It is defined as *the product of the magnitude of charge at one end (Q) and the distance between the charges (r)*.

Mathematically, $\mu = Q \times r$.

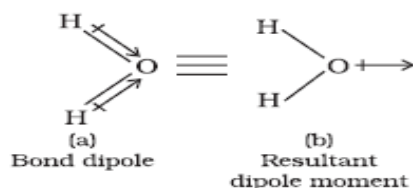
The unit of dipole moment is Coulomb metre (Cm). But it is usually expressed in the unit Debye (D). $1\text{D} = 3.336 \times 10^{-30}$ Cm. Dipole moment is a vector quantity. i.e. it has both magnitude and direction. It is denoted by a small arrow with tail

on the positive centre and head pointing towards the negative centre.

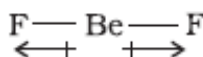
e.g.: HF



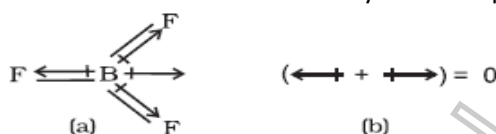
In the case of poly atomic molecules, dipole moment depends on the individual bond dipoles and the spatial arrangement of bonds. Here the dipole moment of the molecule is the vector sum of the bond dipoles of various bonds.
e.g. H₂O



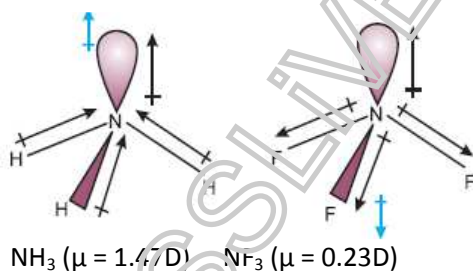
For BeF₂, the net dipole moment is zero, since the two equal bond dipoles are in opposite directions and cancel each other.



In BF₃, the net dipole moment is zero. Here the resultant of any 2 bond dipoles is equal and opposite to the third.



Both ammonia (NH₃) and nitrogen fluoride (NF₃) are pyramidal in shape. *Even though F is more electro negative than H, the net dipole moment of NF₃ is smaller than that of NH₃.* This is because in the case of NH₃, the orbital dipole due to lone pair is in the same direction as the resultant dipole moment of the three N – H bonds. But in NF₃, the orbital dipole is in the opposite direction to the resultant dipole moment of the three N-F bonds. So the dipole moments get partially cancelled.



Covalent character in ionic bonds – Fajans Rules

The partial covalent character of ionic bonds was explained by Fajans in terms of the following rules:

- 1) The smaller the size of the cation and the larger the size of the anion, the greater the covalent character of an ionic bond.
- 2) The greater the charge on the cation, the greater the covalent character of the ionic bond.
- 3) For cations of the same size and charge, the ion with electronic configuration $(n-1)d^n ns^0$ is more polarising than the ion with a noble gas configuration $(ns^2 np^6)$.

The shapes of molecules

Covalent bonds are directional in nature. i.e. they are directed to some specified positions in space. So covalent compounds have definite shapes.

The Valence Shell Electron Pair Repulsion [VSEPR] Theory

This theory was proposed by Sidgwick and Powell and later modified by Nyholm and Gillespie. The important postulates of this theory are:

- 1) The shape of the molecule depends on the number of valence shell electron pairs (VSEPRs) around the central atom.
- 2) The valence shell electron pairs repel each other.
- 3) In order to reduce the repulsion, the electron pairs stay at maximum distance.
- 4) Presence of lone pairs of electron causes distortion in the expected geometry of the molecule.

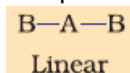
- 5) The repulsion between two lone pairs of electrons is different from those between two bond pairs or between a lone pair and bond pair. The repulsion decreases in the order lone pair - lone pair > lone pair - bond pair > bond pair - bond pair.
- 6) As the angle between the electron pairs increases, the repulsion decreases.

Prediction of geometry of molecules using VSEPR theory

I) Molecules containing only bond pairs of electrons

1) **AB₂ type** (where A is the central atom and B is the no. of bond pairs)

Here there are 2 VSEPs. In order to reduce the repulsion, these electron pairs are arranged at an angle of 180°. Thus the shape of the molecule is linear with bond angle 180°.

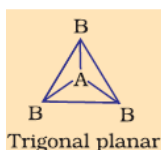


e.g. BeCl₂, HgCl₂ etc.

2) **AB₃ type**

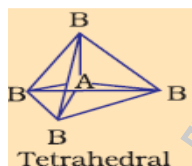
Here there are 3 VSEPs. In order to reduce the repulsion, these electron pairs are arranged at an angle of 120°. Thus the shape of the molecule is planar triangular (trigonal planar) with bond angle 120°.

e.g. BF₃, BCl₃ etc.



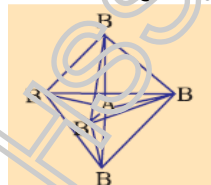
3) **AB₄ type**

Here there are 4 VSEPs. These are arranged at the four corners of a tetrahedron and hence the shape of the molecule is tetrahedral with bond angle 109°28'. e.g.: CH₄, NH₄⁺ etc.



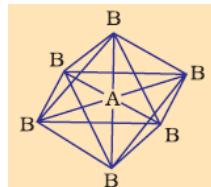
4) **AB₅ type**

Here there are 5 VSEPs. To reduce the repulsion, they are arranged at the five corners of a trigonal bipyramid with bond angles 120° and 90°. E.g.: PCl₅



5) **AB₆ type**

Here there are 6 VSEPs. To reduce the repulsion, they are arranged at the six corners of an octahedron with bond angles 90°. E.g.: SF₆



II) Molecules containing both bond pairs and lone pairs

The presence of lone pairs of electron causes distortion in the shape of the molecules.

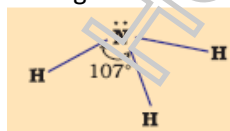
Type of molecule	Total no. of VSEPs	No. of b.ps	No. of l.ps	Shape	e.g.
AB ₂ E	3	2	1	Bent	SO ₂ , O ₃

AB_3E	4	3	1	Trigonal Pyramid	NH_3
AB_2E_2	4	2	2	Bent	H_2O
AB_4E	5	4	1	See-saw	SF_4
AB_3E_2	5	3	2	T-Shape	ClF_3
AB_5E	6	5	1	Square Pyramid	BrF_5
AB_4E_2	6	4	2	Square Planar	XeF_4

Explanation of shapes of ammonia and water molecules by VSEPR theory

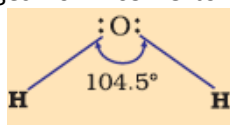
1. NH_3

In ammonia, the central atom N has 5 valence electrons ($7N - 2,5$). Among these electrons, three are used for the formation of bonds with hydrogen atoms and the remaining 2 electrons stay as lone pairs. So there are 4 VSEPs. Hence the expected shape of the molecule is tetrahedral. But due to the presence of lone pairs, the shape is distorted to trigonal bipyramidal and the bond angle changes from $109^\circ 28'$ to 107° .



2. H_2O

In water, the central atom O has 6 valence electrons ($8O - 2,6$). Two of them are used for the formation of bonds with hydrogen atoms and the remaining 4 electrons stay as lone pairs. So there are 4 VSEPs. Hence the expected shape of the molecule is tetrahedral. But due to the presence of 2 lone pairs, the shape is distorted bent or angular or inverted v shape and the bond angle changes from $109^\circ 28'$ to 104.5° .



Orbital overlap concept

Orbital overlapping is the process of partial interpenetration of atomic orbitals. The important characteristics of orbital overlapping are:

1. A covalent bond is formed by the overlapping of half filled atomic orbitals present in the valence shell of atoms.

- The overlapping orbitals should contain electron with opposite spin.
- As a result of overlapping, the electrons get paired and a stable covalent bond is formed.
- The strength of a covalent bond depends on the extent of overlapping. The greater the extent of overlapping, the stronger will be the covalent bond formed.

Types of overlapping

There are two types of orbital overlapping.

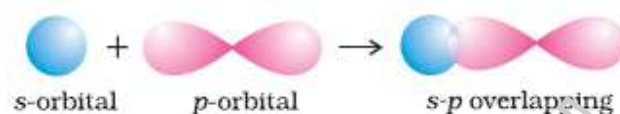
1. **Axial overlapping:**

If the overlapping of atomic orbitals take place *along inter nuclear axis*, it is called axial overlapping or end to end overlapping. A bond formed by axial overlapping is called **sigma (σ) bond**. The electrons present in sigma bond are called sigma electrons. All single bonds are sigma bonds. A sigma bond can be formed by the following ways:

- s-s overlapping: Here the overlapping of two half filled s-orbitals take place along the inter nuclear axis.



- s-p overlapping: It occurs with the overlapping of one half filled s-orbital and one half filled p-orbital.

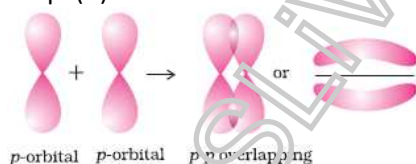


- p-p overlapping: Here two half filled p-orbitals of two atoms overlap.



2. **Lateral overlapping:**

Here the overlapping take place perpendicular to the inter nuclear axis. The bond formed as a result of lateral overlapping is called pi (π) bond. The electrons in pi bond are called π electrons.



A π bond is always present along with σ bonds. A double bond contains one σ bond and one π bond. A triple bond contains one sigma bond and two pi bonds.

A sigma bond is stronger than a pi bond. This is because the extent of overlapping is greater in a sigma bond.

Hybridisation

It is the process of inter mixing atomic orbitals having slightly different energies to form new orbitals having equivalent energy and identical shape. The new orbitals formed are called hybrid orbitals.

Characteristics of hybridisation

- The number of hybrid orbitals formed is equal to the number of atomic orbitals undergo hybridization.
- The hybrid orbitals are always equivalent in energy and in identical shape.
- The hybrid orbitals are more effective in forming stable bonds than the pure atomic orbitals.
- The hybrid orbitals are directed to some fixed positions in space. So the type of hybridization gives the shape of the molecule.

Important conditions of hybridisation

- The orbitals present in the valence shell of the atom are hybridized.
- The orbitals undergoing hybridization should have almost equal energy.
- Promotion of electrons is not an essential condition before hybridisation.
- Completely filled orbitals of valence shell can also take part in hybridisation.

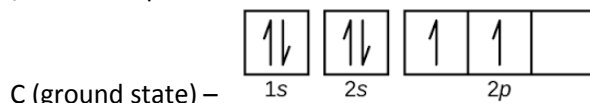
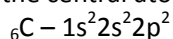
Types of hybridisation

1. **sp^3 hybridisation:** It is the process of inter mixing of one s-orbital and three p-orbitals to form four new orbitals having equivalent energy and shape. The 4 new orbitals formed are called sp^3 hybrid orbitals. They are directed to the four

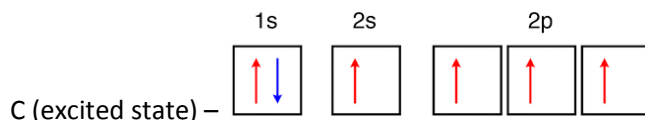
corners of a regular tetrahedron with bond angle $109^{\circ}28'$. Each sp^3 hybrid orbital has 25% s-character and 75% p-character.

e.g. i) . **Formation of methane (CH_4)**

In CH_4 , the central atom C has the electronic configuration



In order to explain the tetra valency of C, it is suggested that one of the electrons of 2s orbital is promoted to 2p orbital.

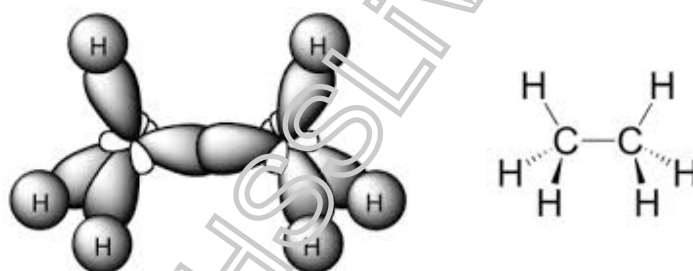


Now, one s-orbital and three p-orbitals undergo sp^3 hybridisation. These sp^3 hybrid orbitals are directed to the four corners of a regular tetrahedron with bond angle $109^{\circ}28'$. Each of these sp^3 hybrid orbitals overlap with 1s orbital of H to form four C-H σ bonds.



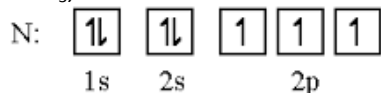
ii) **Formation of ethane (C_2H_6)**

In ethane, each C atom undergoes sp^3 hybridisation. Out of the 4 sp^3 hybrid orbitals, one of each C atom overlaps axially to form a C-C σ bond. The remaining 3 sp^3 hybrid orbitals of each C atom overlap with 1s orbital of H atom to form 6 C-H σ bonds.



iii) **Formation of Ammonia (NH_3) molecule**

In NH_3 , the central atom N has the electronic configuration $1s^2 2s^2 2p^3$.

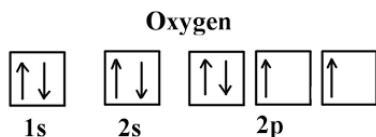


The one s-orbital and three p-orbitals of N undergo sp^3 hybridisation to form 4 sp^3 hybrid orbitals. One of this sp^3 hybrid orbitals is occupied by a lone pair and the other three sp^3 hybrid orbitals overlap with 1s orbital of hydrogen to form 3 N-H bonds. Due to the greater repulsion between lone pair and bond pairs, the shape is distorted to **pyramidal** and the bond angle becomes 107° .

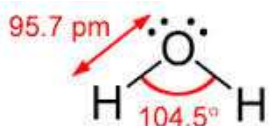
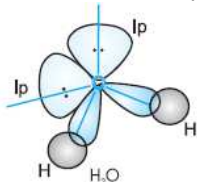


iv) **Formation of water (H_2O) molecule**

In H_2O , the central atom O has the electronic configuration $1s^2 2s^2 2p^4$.



Now the one s-orbital and three p-orbitals of O undergo sp^3 hybridisation to form 4 sp^3 hybrid orbitals. Two of these sp^3 hybrid orbitals are occupied by lone pairs and the other two sp^3 hybrid orbitals overlap with 1s orbital of hydrogen to form 2 O-H bonds. Due to the greater repulsion between lone pairs, the shape is distorted to angular shape or bent structure or inverted 'v' shape and the bond angle becomes 104.5° .

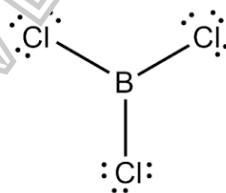


2. **sp^2 hybridisation:** It is the process of inter mixing of one s-orbital and two p-orbitals to form three new orbitals having equivalent energy and shape. The 3 new orbitals formed are called sp^2 hybrid orbitals. They are directed to the three corners of an equilateral triangle. So the shape of the molecule is planar triangular or trigonal planar with bond angle 120° . Each sp^2 hybrid orbitals has 33% s-character and 66% p-character.

e.g. i) **Formation of BCl_3**

Here the central atom B has the electronic configuration $1s^2 2s^2 2p^1$. In the excited state, one of the 2s electrons is promoted to vacant 2p orbital. So the configuration becomes $2s^1 2p^2$.

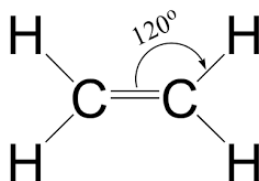
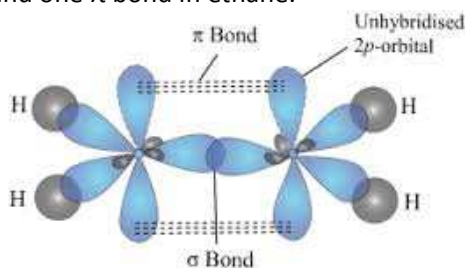
Now one s-orbital and two p-orbitals undergo hybridisation. The 3 hybrid orbitals formed overlap with 2p orbitals of Cl to form 3 B-Cl σ bonds. Since the hybridisation is sp^2 , the shape of the molecule is planar triangular with bond angle 120° .



ii) **Formation of ethane or ethylene (C_2H_4)**

In ethane, each C atom undergoes sp^3 hybridisation. Out of the 3 sp^3 hybrid orbitals, one of each C overlaps axially to form a C-C σ bond. The remaining two sp^3 hybrid orbitals of each C overlap with the 1s orbital of H to form 4 C-H σ bonds.

Now each C atom has one unhybridized p-orbital, which overlaps laterally to form a π bond. Thus there are 5 σ bonds and one π bond in ethane.

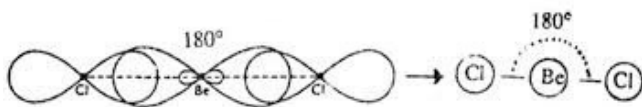


3. **sp hybridisation:** It is the process of inter mixing of one s-orbital and one p-orbital to form two new orbitals having equivalent energy and shape. The 2 new orbitals formed are called sp hybrid orbitals. They are directed in a line. So the shape is linear with bond angle 180° . Each sp hybrid orbitals has 50% s-character and 50% p-character.

e.g. i) **Formation of $BeCl_2$**

In $BeCl_2$, the central atom Be has the electronic configuration $1s^2 2s^2$. In the excited state, one of the 2s electrons is promoted to 2p level. So the configuration becomes $1s^2 2s^1 2p^1$.

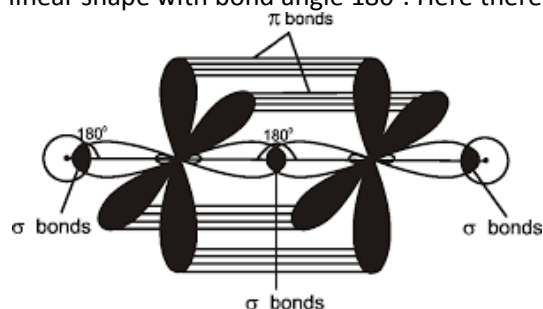
Now one s-orbital and one p-orbital undergo sp hybridisation to form 2 new sp hybrid orbitals. Each of these hybrid orbitals overlaps with the 2p orbitals of Cl to form 2 Be-Cl bonds. So the shape of the molecule is linear with bond angle 180° .



ii) Formation of ethyne or acetylene (C_2H_2)

In acetylene, each C atom undergoes sp hybridisation. Out of the 2 sp hybrid orbitals, one of each C overlaps axially to form a C-C σ bond. The remaining two sp hybrid orbitals of each C overlap with the 1s orbital of H to form 2 C-H σ bonds.

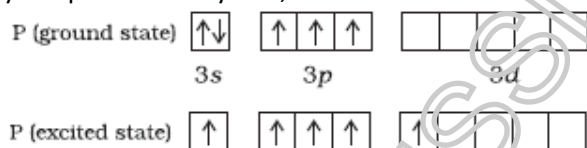
Now each C atom has 2 unhybridized p-orbitals, which overlap laterally to form 2 π bonds. Thus the molecule has linear shape with bond angle 180° . Here there are 3 σ bonds and 2 π bonds in ethyne.



4. **sp^3d hybridisation:** It is the process of inter mixing of one s-orbital, three p-orbitals and one d-orbital to form five new orbitals having equivalent energy and shape. The 5 new orbitals formed are called sp^3d hybrid orbitals. These are directed to the five corners of a regular trigonal bipyramid with bond angles 120° and 90° .

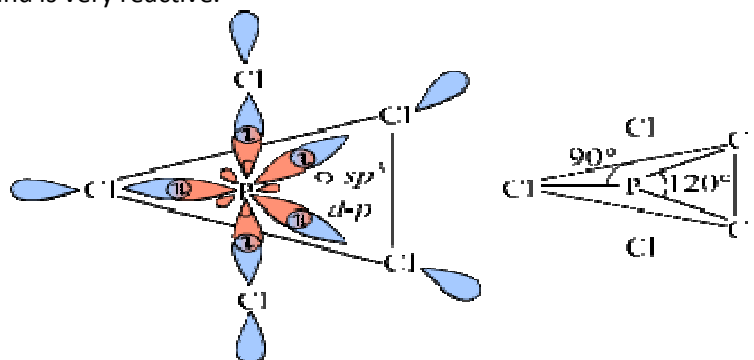
E.g. Formation of PCl_5

In PCl_5 , the central atom P has the electronic configuration $_{15}P - [Ne] 3s^2 3p^3 3d^0$. To satisfy the penta valency of P, one of the 3s electrons is promoted to 3d level.



Now, one s-orbital, three p-orbitals and one d-orbital undergo sp^3d hybridisation. These 5 sp^3d hybrid orbitals are directed to the five corners of a regular trigonal bipyramid with bond angles 120° and 90° .

In PCl_5 , three P-Cl bonds lie in one plane, at an angle of 120° . These three bonds are called equatorial bonds. The other two P-Cl bonds lie one above and one below this plane. They are called axial bonds. The axial bond pairs suffer more repulsion from the equatorial bond pairs. So the axial bond length is greater than the equatorial bond length. So PCl_5 is highly unstable and is very reactive.

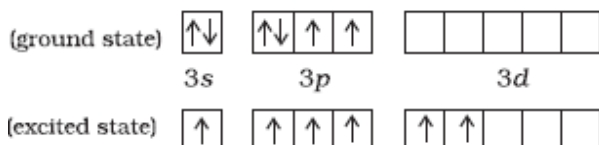


Trigonal bipyramidal structure of PCl_5 .

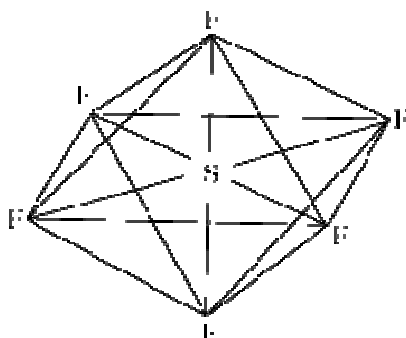
5. **sp^3d^2 hybridisation:** It is the process of inter mixing of one s-orbital, three p-orbitals and two d-orbitals to form six new orbitals having equivalent energy and shape. The 6 new orbitals formed are called sp^3d^2 hybrid orbitals. These are directed to the six corners of a regular octahedron with bond angle 90° .

e.g. Formation of SF_6

In SF_6 the central sulphur atom has the ground state outer electronic configuration $3s^2 3p^4$. In the excited state one electron each from 3s and 3p orbitals are promoted to 3d level.



Now one s-orbital, three p-orbitals and two d-orbitals undergo sp^3d^2 hybridisation. These hybrid orbitals overlap with p-orbitals of fluorine atoms to form 6 S–F sigma bonds. Thus SF_6 molecule has a regular octahedral geometry with bond angle 90° .



Valence bond theory (VBT)

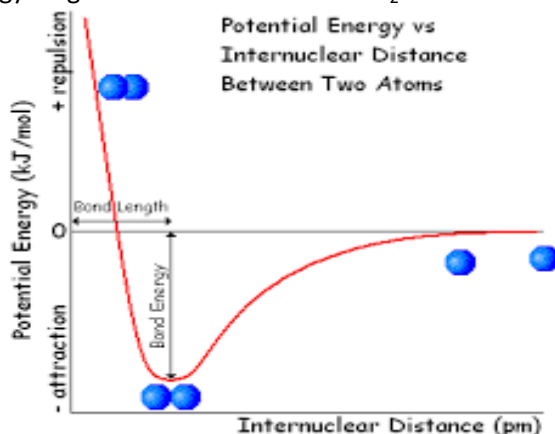
This theory was introduced by Heitler and London and later developed by Linus Pauling in order to explain the shape of molecules theoretically. VBT can be explained by considering the formation of H_2 molecule.

Consider 2 hydrogen atoms A and B with nuclei N_A and N_B and electrons e_A and e_B respectively. When the two atoms are at large distance from each other, there is no interaction between them. So their potential energy is zero. When the two atoms approach each other, new attractive and repulsive forces begin to operate.

Attractive forces arise between nucleus of one atom and electron of other atom i.e., $N_A - e_B$ and $N_B - e_A$. Similarly repulsive forces arise between electrons of two atoms i.e., $e_A - e_B$, and the nuclei of two atoms $N_A - N_B$. Attractive forces bring the two atoms close to each other whereas repulsive forces push them away.

Experimentally it has been found that the magnitude of new attractive force is more than the new repulsive forces. So the two atoms approach each other and potential energy decreases. At a particular stage, the net attractive force balances the net repulsive forces and the energy becomes minimum. At this stage, the hydrogen atoms are said to be bonded together to form a stable molecule. The distance between the two atoms at this stage is called **bond length** (74 pm). The amount of energy liberated at this stage is called **bond enthalpy** (435.8 kJ/mol)

The potential energy diagram for the formation of H_2 molecule is as shown below:



Molecular Orbital Theory

This theory was developed by F.Hund and R.S Mulliken. The important postulates of this theory are:

- 1) In molecules, the electrons are present in some special type of orbitals called molecular orbitals (M.Os).
- 2) The atomic orbitals (A.Os) of comparable energy and proper symmetry combine to form molecular orbitals.
- 3) Atomic orbitals are monocentric, while molecular orbitals are polycentric. i.e. electrons present in atomic orbitals are attracted by only one nucleus. While the electrons present in molecular orbitals are attracted by more than one nuclei.
- 4) The number of molecular orbitals formed = the number of atomic orbitals combined. i.e. if 2 atomic orbitals combined, 2 molecular orbitals are formed. One is called bonding molecular orbital (BMO) and the other is called anti-bonding molecular orbitals (ABMO)
- 5) The BMO has lower energy and greater stability than the corresponding ABMO.
- 6) The molecular orbitals give the electron probability distribution around a group of nuclei.
- 7) The molecular orbitals are filled according to 3 rules – Aufbau principle, Pauli's exclusion principle and Hund's rule.

Formation of molecular orbitals – Linear Combination of Atomic Orbitals (LCAO) method

Molecular orbitals are formed by the combination of atomic orbitals by an approximate method known as Linear Combination of Atomic Orbitals (LCAO). According to this theory, the combinations of atomic orbitals take place by addition and subtraction of wave functions of atomic orbitals. The M.O formed by the addition of A.Os is called the bonding molecular orbital (BMO) and by the subtraction of A.Os is called the anti-bonding molecular orbitals (ABMO).

The electron density in a BMO is located between the nuclei of the bonded atoms. So the repulsion between the nuclei is very low. Therefore a BMO always possess lower energy than the combining A.Os. While in the case of an ABMO, most of the electron density is located away from the space between the nuclei. There is a nodal plane between the nuclei and hence the repulsion between the nuclei is high. So an ABMO possess higher energy than the combining A.Os. ABMO is denoted by using an asteric (*) mark.

Conditions for the combination of atomic orbitals

The combination of A.Os to form M.Os takes place only if the following conditions are satisfied:

1. The combining A.Os must have the same or nearly the same energy.
2. The combining A.Os must have the same symmetry about the molecular axis.
3. The combining A.Os must overlap to the maximum extent.

Types of molecular orbitals

M.Os of diatomic molecules are designated as σ (sigma), π (Pi), δ (delta) etc. the sigma M.Os are symmetrical about the bond axis, while the pi M.Os are not symmetrical.

Linear combination of two 1s atomic orbitals produces two M.Os – a BMO σ_{1s} and an ABMO σ^*_{1s} .

Similarly linear combination of two 2s atomic orbitals produces two M.Os – σ_{2s} and σ^*_{2s} .

If z-axis is taken as the inter nuclear axis, linear combination of two $2p_z$ orbitals produces two sigma M.Os σ_{2p_z} and $\sigma^*_{2p_z}$.

While the combination of $2p_x$ and $2p_y$ orbitals produce M.Os which are not symmetrical about the bond axis. So two $2p_x$ orbitals produces 2 sigma M.Os – π_{2p_x} and $\pi^*_{2p_x}$ and two $2p_y$ orbitals produce 2 M.Os – π_{2p_y} and $\pi^*_{2p_y}$.

Energies of various M.Os

The various M.Os are filled in the increasing order of their energies (Aufbau Principle). The increasing order of energy is:

$$\sigma_{1s} < \sigma^*_{1s} < \sigma_{2s} < \sigma^*_{2s} < (\pi_{2p_x} = \pi_{2p_y}) < \sigma_{2p_z} < (\pi^*_{2p_x} = \pi^*_{2p_y}) < \sigma^*_{2p_z}$$

For O_2 , F_2 and Ne_2 , the order is:

$$\sigma_{1s} < \sigma^*_{1s} < \sigma_{2s} < \sigma^*_{2s} < \sigma_{2p_z} < (\pi_{2p_x} = \pi_{2p_y}) < (\pi^*_{2p_x} = \pi^*_{2p_y}) < \sigma^*_{2p_z}$$

Bond Order

It is defined as *the half of the difference between the number of bonding electrons (N_b) and the number of anti-bonding electrons (N_a)*.

$$\text{i.e. Bond order (B.O)} = \frac{1}{2} [N_b - N_a]$$

A molecule is stable only if the bond order is positive. (i.e. $N_b > N_a$). a negative bond order (i.e. $N_b < N_a$ or $N_b = N_a$) means an unstable molecule.

For a single bond, B.O = 1, for a double bond B.O = 2 and so on. Bond order gives an approximate measure of the bond length. In general, **as the bond order increases, bond length decreases and bond enthalpy increases.**

Magnetic nature

If all the M.Os in a molecule are doubly occupied, the substance is diamagnetic. i.e. that substance is repelled by an external magnetic field. If one or more M.Os are singly occupied, it is paramagnetic. i.e. it is attracted by an external magnetic field. E.g. O_2 molecule.

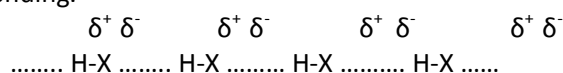
Molecular orbital Diagram

The representation of various M.Os in the increasing order of energy is called M.O diagram.

Hydrogen Bonding

The weak attractive force between Hydrogen atom of one molecule and electronegative atom (like F, O or N) of the same or different molecule is termed as Hydrogen bond. It is weaker than a covalent bond but stronger than van der Waal's force. It is represented by dotted line (.....).

Cause of H bonding: When H is bonded to a strongly electronegative atom X, the shared electron pair is shifted more towards X. So H atom gets a slight positive charge (δ^+) and the electronegative atom gets a slight negative charge (δ^-). This results in the formation of a polar molecule. The electrostatic force of attraction between these polar molecules is termed as H-bonding.

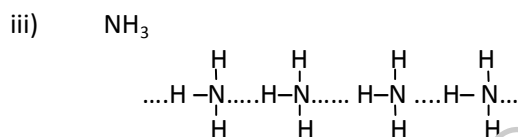
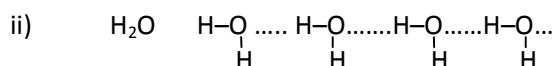


Types of H bond

There are two types of H bonds- inter molecular H-bonding and intra molecular H-bonding.

- 1) **Inter molecular H bonding:** It is the H bond formed by H atom of one molecule and the electronegative atom of another molecule.

e.g. i) H bonding in HF



Inter molecular H bonding influences the physical properties of the compounds. For example water (H_2O) is a liquid with high boiling point but hydrogen sulphide (H_2S) is a gas. This is because in water inter molecular H bonding is possible which is not possible in H_2S .

2) **Intra molecular H bonding:** It is the H bond formed between H atom and the electronegative atom of the same molecule.

e.g. H bonding in ortho-nitrophenol

