01 Chemical Bonding and Molecular Structure

Introduction:

- It is well known fact that except inert gases, no other element exists as independent atoms under ordinary condition.
- Most of the elements exist as molecules which are cluster of atoms. How do atoms combine to form molecules and why do atoms form bonds? Such doubts will be discussed in this chapter.
- A molecule will only be formed if it is more stable and has a lower energy, than the individual atoms.

Chemical Bond:

- A force that acts between two or more atoms to hold them together as a stable molecule.
- It is union of two or more atoms involving redistribution of $e^{\ominus}$ among them.
- This process accompanied by decrease in energy.
- **Decrease in energy α Strength of the bond.**
- Therefore, molecules are more stable than atoms.

Cause of Chemical Combination:

Tendency to acquire minimum energy:

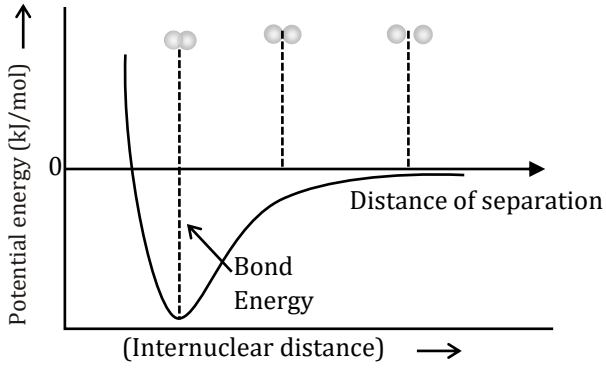
(a) When two atoms approach towards each other, Nucleus of one atom attracts the electrons of another atom.

(b) Two nuclei and electrons of both the atoms repel each other.

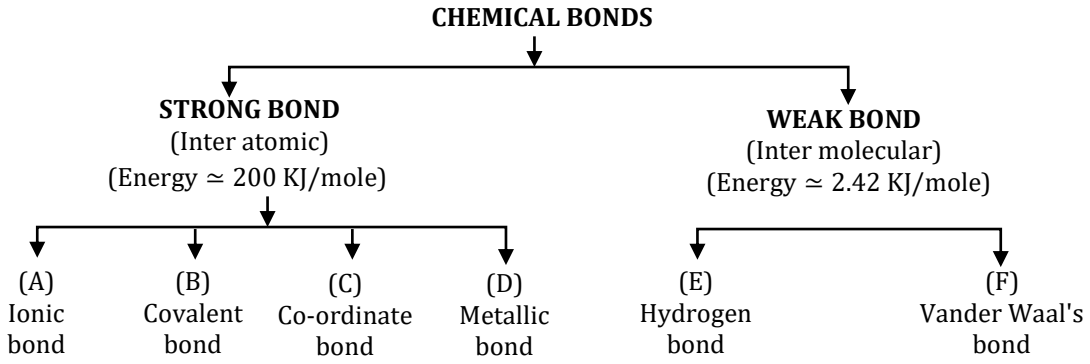
(c) If net result is attraction, the total energy of the system (molecule) decreases and a chemical bond is formed.

(d) So, **Attraction α 1/energy α Stability.**

(e) Bond formation is an exothermic process (ΔH = negative)



Classification of Bonds:



Ionic or Electrovalent bond:

(a) The chemical bond formed between two or more atoms as a result of the complete transfer of one or more electrons from one atom to another is called Ionic or electrovalent bond.

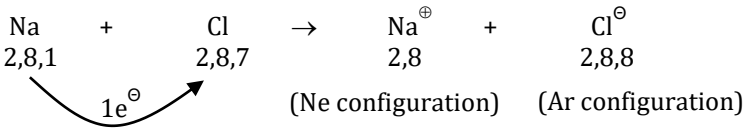
(b) Electropositive (metal) atom loses electron

(c) Electronegative (non-metal) atom gains electron

(d) Electrostatic force of attraction between cation and anion is called ionic bond or electrovalent bond.

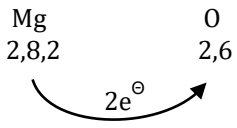
Electronegativity difference ∝ nature of ionic bond.

e.g. IA and VIIA group elements form maximum ionic compound.



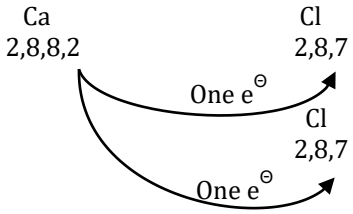
Total number of electrons lose or gained is called electro valency.

Example –

(1) 

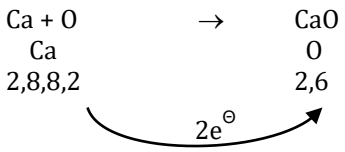
Electro valency of Mg = 2

Electro valency of O = 2

(2) 

electro valency of Ca = 2

electro valency of Cl = 1

(3) 

Electro valency of Ca = 2

Electro valency of O = 2

During formation of ionic bond octet will be completed.

Representation of formula of compounds:

(1) Write the symbols of the ions side by side in such a way that positive ion is at the left and negative ion is at the right as $A^{\oplus}B^{\ominus}$

(2) Write their electro valency in figure at the top of each symbol as A^x B^y

(3) Now apply Criss cross rule as 

, i.e. formula AyBx.

Example: Calcium chloride

$= Ca^{2\oplus}Cl^{\ominus}$

(c) Lattice energy (L.E.) ;

Amount of energy released when one mole of crystal lattice is formed from its constituents gaseous ions or amount of energy required to break one mole of crystal lattice into its constituents gaseous ion is known as lattice energy.

Higher lattice energy → Greater will be the stability or strength of ionic compound.

Factors affecting lattice energy:

(a) Magnitude of charge → $U \propto q_1 q_2$ (charge on ions)

Lattice energy α Magnitude of charge

NaCl	$MgCl_2$	$AlCl_3$
$Na^{\oplus}$	$Mg^{2\oplus}$	$Al^{3\oplus}$

$\longrightarrow$

– Charge of anion constant
– Lattice energy increases
– Charge of cation increases

(b) Size of Cation :- Lattice energy $-\frac{kq_1q_2}{r}$

LiCl	NaCl	KCl	RbCl	CsCl
$Li^{\oplus}$	$Na^{\oplus}$	$K^{\oplus}$	$Rb^{\oplus}$	$Cs^{\oplus}$

$\longrightarrow$

– Size of cation increasing
– Size of anion is constant
– Lattice energy decreases.

Conditions for Forming Ionic Bonds:

Formation of Ionic bond depends upon these three factors –

(a) Ionisation energy (I.E.):

Amount of energy required to remove an electron from the outermost orbit of an isolated gaseous atom to form the +ve ion or cation. (energy absorbed)

Lesser Ionisation energy → Greater tendency to form cation.

e.g. $\left.\begin{matrix} Na^{\oplus} > Mg^{2\oplus} > Al^{3\oplus} \\ Cs^{\oplus} > Rb^{\oplus} > K^{\oplus} > Na^{\oplus} > Li^{\oplus} \end{matrix}\right\}$ Cation formation tendency

(b) Electron affinity (E.A.):

Amount of energy released when an electron is added to an isolated gaseous atom to form –ve ion (anion) energy released.

Higher electron affinity → Greater tendency to form anion

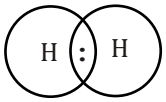
$Cl^{\ominus} > F^{\ominus} > Br^{\ominus} > I^{\ominus}$

$F^{\ominus} > O^{2\ominus} > N^{3\ominus}$

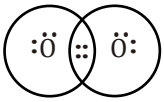
(c) Lattice Energy (U) : Higher lattice energy ∝ strength of ionic bond.

Covalent Bond:

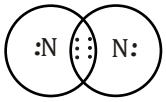
- A covalent bond is formed by the mutual sharing of electrons between two atoms of electro negative elements to complete their octet. (Except H which completes its duplet)



H_2 molecule



O_2 molecule

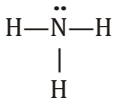


N_2 molecule

H — H O = O N ≡ N

- The shared pair of electrons should have opposite spins, and are localised between two atoms concerned.
- Sharing of electrons may occurs in three ways –

	No. of electrons shared	Electron pair	Bond. between two atoms
(1)	2	1	Single bond (—)
(2)	4	2	Double bond (═)
(3)	6	3	Triple bond (≡)

Examples –  Three single bonds (not triple bond)

N ≡ N Triple bond. (not three single bond)

O═ O Double bond (Not two single bond)

H — O — H (Two single bonds.)

Orbital Concept of Covalent Bond:

According to this concept:

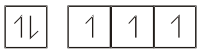
- One orbital can accommodate maximum 2 electrons with opposite spins ⇅.
- Half-filled orbital or unpaired electron orbital accepts one electron from another atom, to complete its orbital.
- Tendency to complete orbital or to pair the electron is an essential condition of covalent bond.
- Completion of octet is not the essential condition of covalent bond.
- **Covalency** : It is the number of covalent bonds which an atom makes in a molecule, either in ground state or in excited state.

Variable Valency in Covalent Bonds:

- Variable valencies are shown by those elements which have empty orbitals in outermost shell.
- Lone pair electrons get excited in the subshell of the same shell to form the maximum number of unpaired electrons. Maximum covalency is shown in excited state.
- 3, 4, 5, 6 period elements due to the presence of vacant d-orbital in the presence of highly electro negative elements such as (F, O, Cl) can show variable valencies.
- The energy required for excitation of electrons is called promotion energy/excitation energy
- **Promotion rule** – Excitation of electrons takes place in the same orbit.

Example –

(a) Nitrogen → Ground state

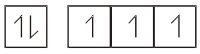


Covalency 3 (NCl_3)

Nitrogen → No excited state

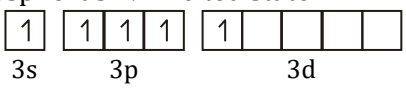
Not possible due to absence of vacant orbital that's why (NCl_5) does not exist

(b) Phosphorus → Ground state



Covalency 3 (PCl_3)

Phosphorus → Excited state



Covalency – 5 (PCl_5)

Note :

NCl_3 — exists

NCl_5 — doesn't exists
(due to absence of d-orbitals in Nitrogen.) While PCl_3 and PCl_5 both exists because 3d orbitals are present in phosphorus.

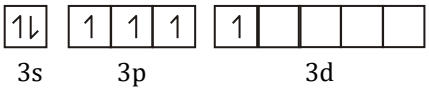
OF_2 — exists, but OF_4 and OF_6 doesn't exists due to absence of d-orbitals While SF_4 and SF_6 exists due to presence of d-orbital, present in its valence shell.

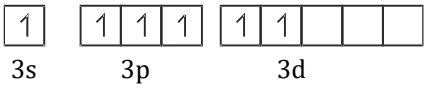
- It can explain existence of molecules.

(c) Sulphur → Ground state.

Covalency - 2(SF_2)

Sulphur → Excited state

1st excited state  Covalency - 4 (SF_4)

2nd excited state  Covalency - 6 (SF_6)

So variable covalency of S is 2, 4, & 6.

Note :

It is not necessary that only 3, 4, 5, 6 period elements forms their compound in excited state but 2 period elements also forms compound in excited state.

Example - Be, B, C forms most of their compound in excited state.

(1) Be – $1s^2, 2s^2$

Ground state ⇅ | | | Covalency = 0

Excited state ↑ | ↑ | | Covalency = 2

(2) C = $1s^2, 2s^2, 2p^2$

Ground state ⇅ | ↑ | ↑ | Covalency = 2

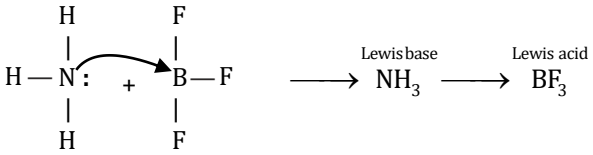
Excited state ↑ | ↑ | ↑ | ↑ Covalency = 4

Co-ordinate bond (Dative bond):

(a) It is a covalent bond in which the shared e– pair come from one atom is called coordinate bond.

(b) Atom which provide electron pair for sharing is called donor (Lewis base).

(c) Other atom which accepts electron pair is called acceptor (Lewis acid). That is why it is called donor-acceptor or dative bond.

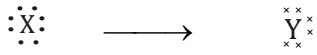


BF_3 is electron deficient compound.

(d) Necessary conditions for the formation of coordinate bond are -

(a) Octet of donor atom should be complete and should have atleast one lone pair of electron.

(b) Acceptor atom should have vacant orbital to accommodate L.P.

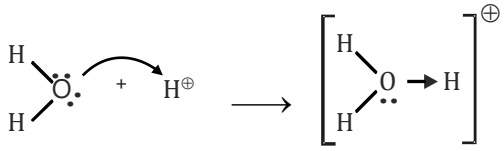
eg. :-  or X ⟶ Y

Protonation (Addition of $H^{\oplus}$ ion)

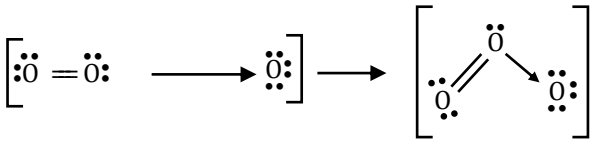
Example : $NH_4^{\oplus}$ (Ammonium ion)

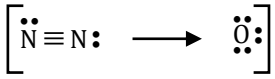
$NH_3 + H^{\oplus} \rightarrow NH_4^{\oplus}$

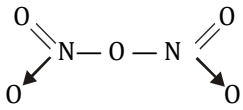
Example : $H_3O^{\oplus}$ (Hydronium ion)

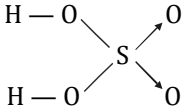


Other examples of co-ordinate bond

O_3 ; 

N_2O ; 

N_2O_5 ; 

H_2SO_4 ; 

Compounds in which Ionic, covalent and co-ordinate bonds are present, are as follows -
NH_4Cl, Na_3PO_4, KNO_3, etc.

Lewis Dot Structures or Lewis Symbols:

According to Lewis in the formation of a molecule, only the outer most shell electrons take part in chemical combination & they are called valence electrons. The inner shell electrons are well protected and are generally not involved in the combination process. Lewis introduced simple notations to represent valence electrons in an atom. These notations are called Lewis symbols or Lewis dot structure.

Lewis symbols for atoms and monoatomic ions :

Lewis symbol for second period elements are :

Number of dots around the symbol represents the number of valence electrons.

Lewis symbol for some anions are

How to draw the Lewis electron dot/Bond line structure of inorganic covalent compounds:

1. (i) First of all, identify the central atom in the given species. Central atom in a given molecule/ion is usually that atom which is least electronegative.

(ii) Hydrogen can't be central atom as its covalency is one.

(iii) Sometimes the central atom is that atom which is less in number.

(iv) Sometimes the central atom in the given molecule/ion can't be decided on the basis of electronegativity or number of atoms (less). In such cases, that atom is central atom which appears in central position of given formula of molecule/ion.

To make it more clear, central atoms in the following species are starred (*).

$\Rightarrow$ $\overset{*}{C}H_4$, $\overset{*}{N}H_3$, $H_2\overset{*}{O}$, $\overset{*}{C}H_2Cl_2$, $\overset{*}{C}HF_3$

(Note-that electronegativity of H is less than that of central atom).

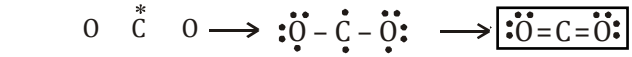
$\Rightarrow$ $\overset{*}{C}O_2$, $\overset{*}{S}O_2$, $\overset{*}{S}O_3$, $\overset{*}{S}OCl_2$, $\overset{*}{P}SCl_3$

$\Rightarrow$ $\overset{*}{O}Cl_2$, $\overset{*}{O}Br_2$

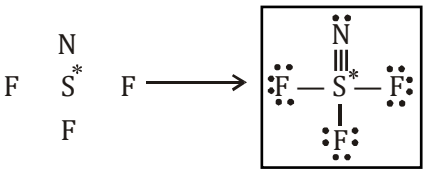
(Note that oxygen is more electronegative, but it is less in number)

$\Rightarrow$ $(\overset{*}{S}CN)^-$, (order of appearance)

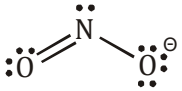
2. Surrounding atoms are the atoms which are directly bonded to central atom.
3. Arrange the surrounding atoms around the central atom and first form single bond between all surrounding atom with central atom.
4. Always make sure that octet of all the surrounding atoms is complete. If it is not achieved by forming single bond, then try to make the double bond or triple bond between central atom and surrounding atom, as required to complete the octet of surrounding atoms.
   e.g., $\underline{CO_2}$



   $\underline{SNF_3}$

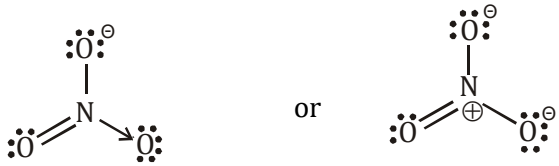


5. After the bond formation, represent the lone pair of electrons on central atom as well as on surrounding atoms.
6. Make sure that, in the structure you have made, the octet of the all surrounding atoms must be completed.
7. If the central atom belongs to second period, it can have ≤ 8 (max.) electrons i.e. ≤ 4 bonds, but never greater than 8 electrons (i.e. > 4 bonds).
8. However, if the central atom belongs to third or lower period it can have ≥ 8 electrons.
9. At last verify the covalency of central atom.
10. **Lewis Structure of ions:**
    Distribute the negative charge on surrounding atom in such a way that octet of none of the surrounding atom is complete before the bond formation with central atom. If however, the octet of surrounding atom is complete by making it non negatively charged (particularly in case of halogen which contain seven valence electron), then such surrounding atom will attach itself with central atom through a co-ordinate covalent bond.

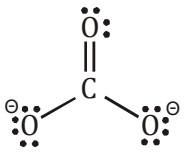


    But the above structures of $NO_3^{\ominus}$ is incorrect as the central nitrogen belongs to second period, it can never form five covalent bond i.e., it can't have more than 8 electrons, so its actual structure is

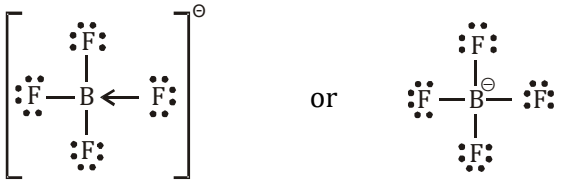
1. $NO_3^{\ominus}$



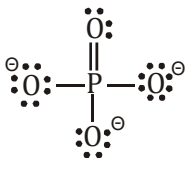
2. $CO_3^{2\ominus}$



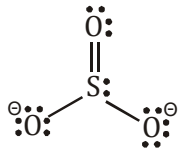
3. $BF_4^{\ominus}$



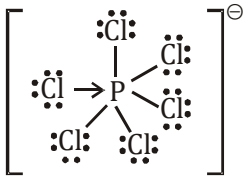
4. $PO_4^{3\ominus}$



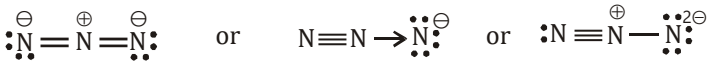
5. $SO_3^{2\ominus}$



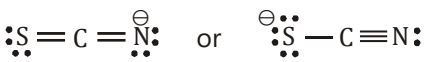
6. $PCl_6^{\ominus}$



7. $NO_3^{\ominus}$



8. $SCN^{\ominus}$



Formal Charge:

Lewis dot structures, in general, do not represent the actual shapes of the molecules. In case of polyatomic ions, the net charge is possessed by the ion as a whole and not by a particular atom. It is, however, feasible to assign a formal charge on each atom.

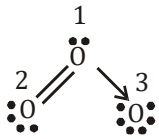
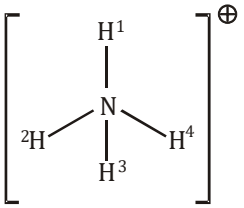
Formal Charge : $Q_F = N_A - N_{L.P.} - \frac{1}{2} N_{B.P.}$

Where :

N_A = Total number of valence electron in the free atom

$N_{L.P.}$ = Total number of non bonding (lone pair) electrons

$N_{B.P.}$ = Total number of bonding(shared) electrons

Molecule	Structure	Formal Charge
O_3		$O(1) = 6 - 2 - \frac{1}{2}(6) = +1$ $O(2) = 6 - 4 - \frac{1}{2}(4) = 0$ $O(3) = 6 - 6 - \frac{1}{2}(2) = -1$
CO		$C = 4 - 2 - \frac{1}{2}(6) = -1$ $O = 6 - 2 - \frac{1}{2}(6) = +1$
$NH_4^{\oplus}$		$N = 5 - 0 - \frac{1}{2}(8) = +1$ On each H $= 1 - 0 - \frac{1}{2}(2) = 0$

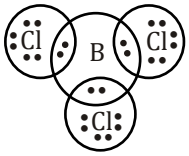
- Formal charges help in the selection of the lowest energy structure from a number of possible Lewis structures for a given species.

Exception of Octet Rule (Failure):

(a) Incomplete octet molecules or electron deficient molecules or hypovalent.

Compound in which octet is not complete in outer most orbit of central atom.

Example - Halides of IIIA groups, BF_3, $AlCl_3$, BCl_3, hydride of III A/13th group etc.



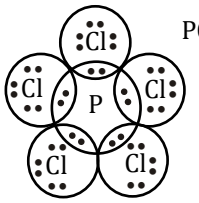
[In BCl_3 Boron has only 6 electrons]

Other examples – $BeCl_2$ ($4e^{\ominus}$), $HgCl_2$ ($4e^{\ominus}$), $Ga(CH_3)_3$ ($6e^{\ominus}$)

(b) Expansion of octet or electron efficient molecules or hypervalent

Compound in which central atom has more than $8e^{\ominus}$ in outermost orbit.

Example - In PCl_5, SF_6, IF_7, the central atom P, S and I contain 10, 12, and 14 electrons respectively.



PCl_5

(c) Pseudo inert gas configuration :-

Cations which contains 18 electrons in outermost orbit

Ex. $Ga^{3\oplus}$, $Cu^{\oplus}$, $Ag^{\oplus}$, $Zn^{2\oplus}$, $Cd^{2\oplus}$, $Sn^{4\oplus}$, $Pb^{4\oplus}$ etc.

Electronic configuration of Ga - $1s^2,2s^22p^6,3s^23p^63d^{10},4s^24p^1$

Electronic configuration of $Ga^{3\oplus}$ - $1s^2,2s^2\ 2p^6,\ \underbrace{3s^23p^63d^{10}}_{18e^{\ominus}}$

(d) Odd electron molecules :-

In Which central atom have an unpaired electron or odd no ($7e^{\ominus}$, $11e^{\ominus}$ etc) of electrons in their outer most shell.

e.g. NO, NO_2, ClO_2 etc.

Resonance:

When a molecule cannot be completely represented by a single Lewis structure but it's characteristic properties can be described by two or more different structures, with similar energy position of nuclei, bonding and non-bonding pairs of electrons, then the true structure is said to be resonance hybrid of these structures. The phenomenon is called resonance and different contributing structures are called resonating structures or canonical structures.

- Resonance stabilizes the molecule as the energy of the resonance hybrid is less than the energy of any single canonical structure.
- Resonance averages the bond characteristics as a whole.
- The canonical forms have no real existence.

Resonance Energy:

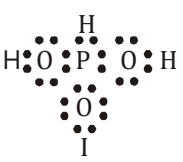
Energy difference between most stable resonating structure and resonance hybrid structure is called resonance energy.

Rules For Writing Resonating Structures:

To explain the characteristics of a molecule, a number of resonating structures may be written.

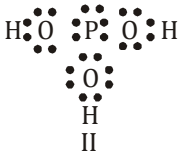
(1) The contributing structure having similar energy contribute equally to the resonance hybrid. The canonical form having higher energies contribute to a lesser extent to the resonance hybrid.

(2) The contributing structures should have the same atomic positions. They should differ only in the position of electrons. For Example, the following two structures of phosphorus acid (H_3PO_3) are not resonating structures because they have different positions of atoms in the two structures.



I

&



II

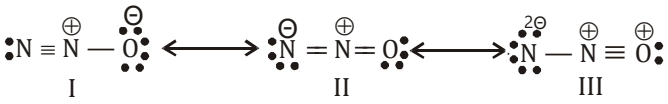
are not resonating structures.

(3) The contributing structures should have the same number of unpaired electrons.

(4) The contributing structures should not differ much in energy.

(5) Contributing structures should be so written that the negative charge resides on more electronegative element and positive charge resides on less electronegative element.

(6) In contributing structures, like charges, should not reside on adjacent atoms. This means that contributing structures should be so written that unlike charges reside on neighbouring atoms while like charges are separated as far apart possible. For example, resonating structures of N_2O may be written as follows :

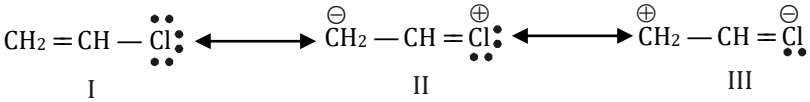


I II III

In this case structure (III) is not feasible because it place a positive charge on the electronegative oxygen atom and also has same positive charges on the adjacent nitrogen atom.

(7) A resonating structure that violate octet Rule will be least stable

Example :



I II III

Order of stability

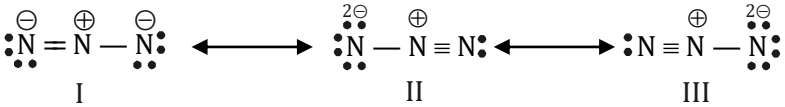
I > II > III

Bond order : Number of bonds between two atoms is called bond order.

Resonance Structure of Some Molecules/Ions:

(i) Azide ion, $N_3^{\ominus}$:

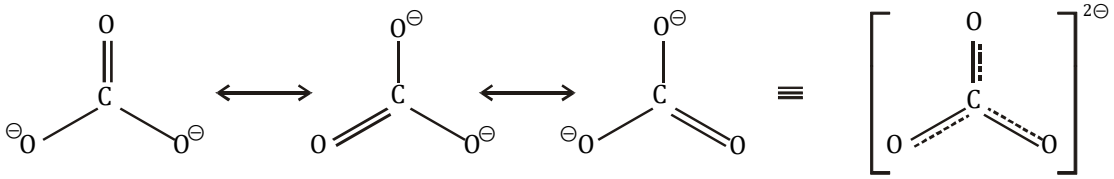
The azide ion may be represented as –



I II III

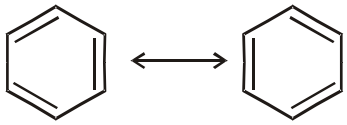
The structures II and III contribute equally and the molecule has almost double bond character in each N–N bond.

(ii) Carbonate, $CO_3^{2\ominus}$



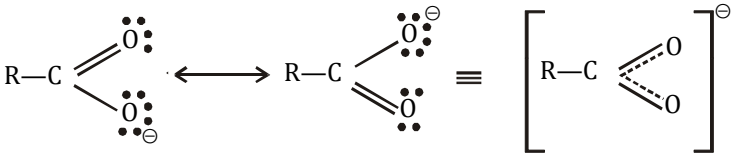
B.O. = 1.33

(iii) Benzene, C_6H_6



BO = 1.5

(iv) Carboxylate ion, $RCOO^{\ominus}$



Bond order $= \frac{2+1}{2} = \frac{3}{2} = 1.5$

Valence bond theory (VBT):

(A) It was presented by Heitler & London to explain how a covalent bond is formed.
It was extended by Pauling & Slater.

(B) The main points of theory are –

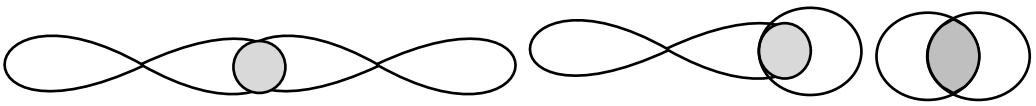
(a) To form a covalent bond overlapping occurs between half-filled valence shell orbitals of the two atoms.
(b) Orbitals come closer to each other from the direction in which there is maximum overlapping
(c) So covalent bond has directional character.
(d) Strength of covalent bond $\propto$ extent of overlapping.
(e) Extent of overlapping depends on two factors.

(i) Nature of orbitals –

(a) As the value of n increases, bond strength decreases.
1s - 2p > 2s - 2p > 3s - 3p

(b) p, d and f are directional orbitals $\rightarrow$ more overlapping
s-orbital $\rightarrow$ non-directional – less overlapping
The bond is formed by the overlapping of directional orbital is more stronger than the bond formed by overlapping of non-directional orbital.

p–p > s–p > s–s



p - p p–s s–s

(c) If n is same 2p - 2p > 2s - 2p > 2s - 2s

(ii) Nature of overlapping – Co-axial overlapping - extent of overlapping more.
Collateral overlapping - extent of overlapping less

Order of strength of Co - axial overlapping – p - p > s - p > s – s

Types of Overlapping and Nature of Covalent Bonds:

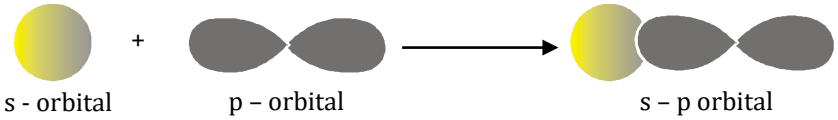
The covalent bond may be classified into following types depending upon the types of overlapping :-
(i) sigma (σ) bond (ii) pi (π) bond (iii) delta (δ) bond

(i) Sigma (σ) bond:

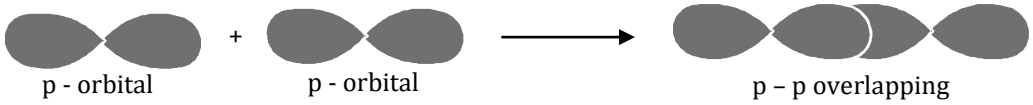
This type of covalent bond is formed by the end to end (head on or axial) overlap of bonding orbitals along the internuclear axis. This can be formed by any one of the following types of combinations of atomic orbitals.

- s-s overlapping : In this case, there is overlap of two half filled s-orbitals along the internuclear axis as shown below

- s-p overlapping: This type of overlap occurs between half filled s-orbital of one atom and half filled p-orbital of another atom.



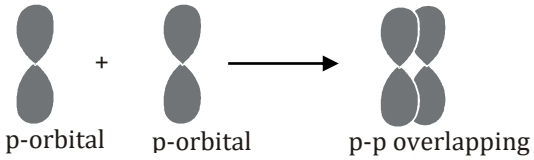
- p-p overlapping : This type of overlap takes place between half filled similar p-orbitals of the two approaching atoms.



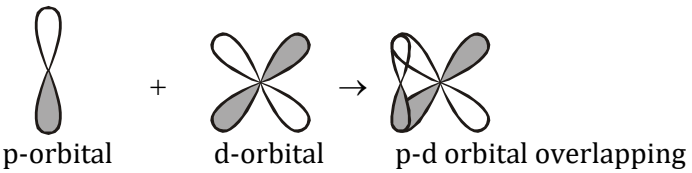
(ii) pi (π) bond:

In the formation of π bond the atomic orbitals overlap in such a way that their axis remains parallel to each other and perpendicular to the internuclear axis. The orbitals formed due to sidewise overlapping consists of two saucer type charged clouds above and below the plane of the participating atoms.

(a) p_π–p_π

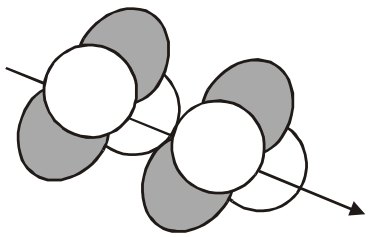


(b) p_π–d_π



(iii) delta (δ) bond:

Delta (δ) bond are the covalent bonds where four lobes of d-orbital of one atom overlap with four lobes of the similar d-orbital of other atom. Except d_{z^2} all d orbitals can form δ bond.



Atomic orbitals	Internuclear axis	Type of covalent bond
$s + p_x$	x axis	σ
	y axis	×
	z axis	×
$s + p_y$	x axis	×
	y axis	σ
	z axis	×
$s + p_z$	x axis	×
	y axis	×
	z axis	σ
$p_x + p_x$	x axis	σ
	y axis	π
	z axis	π
$p_y + p_y$	x axis	π
	y axis	σ
	z axis	π
$p_z + p_z$	x axis	π
	y axis	π
	z axis	σ
$p_x + p_y$	x axis	×
	y axis	×
	z axis	×
$p_y + p_z$	x axis	×
	y axis	×
	z axis	×
$p_x + p_z$	x aixs	×
	y axis	×
	z axis	×
$p_x + d_{xy}$	x axis	×
	y axis	π
	z axis	×
$p_x + d_{yz}$	x axis	×
	y axis	×
	z axis	×
$p_x + d_{zx}$	x axis	×
	y axis	×
	z axis	π
$p_y + d_{xy}$	x axis	π
	y axis	×
	z axis	×
$p_y + d_{yz}$	x axis	×
	y axis	×
	z axis	π
$p_y + d_{zx}$	x axis	×

	y axis	×
	z axis	×
$p_z + d_{xy}$	x axis	×
	y axis	×
	z axis	×
$p_z + d_{yz}$	x axis	×
	y axis	π
	z axis	×
$p_z + d_{zx}$	x axis	π
	y axis	×
	z axis	×
$d_{xy} + d_{xy}$	x axis	π
	y axis	π
	z axis	δ
$d_{yz} + d_{yz}$	x axis	δ
	y axis	π
	z axis	π
$d_{xz} + d_{xz}$	x axis	π
	y axis	δ
	z axis	π

Strength of sigma and π-Bonds:

Basically the strength of a bond depends upon the extent of overlapping- In case of sigma bond, the overlapping of orbitals takes place to a larger extent. Hence, it is stronger as compared to the π-bond where the extent of overlapping occurs to a smaller extent. Further, it is important to note that pi bond between two atoms is formed in addition to a sigma bond. It is always present in the molecules containing multiple bond (double or triple bonds)

Advantages of VBT:

- It explain various bond characteristics e.g., bond length, bond strength.
- It explains the quantitative relationship between the extent of overlapping and bond dissociation energy.
- This theory accounts for shape and nature of bonding of the molecule whose covalency is not according to the number of half-filled orbitals present in the ground state.
- This theory redefined the stability of molecules e.g. BF_3, $AlCl_3$, PCl_5, SF_6 etc which are exception to octet rule.

Disadvantages of VBT:

- According to this theory three bond angle in CH_4 should be 90°, as these are formed by p–p overlapping, but actually it has 109°28 angles. In NH_3 & H_2O, angle should be 90°. This is in disagreement with the actual bond angles of 107° & 104.5° in NH_3 & H_2O molecules respectively.
- In order to explain the characteristic geometrical shapes of polyatomic molecules like CH_4, NH_3, H_2O etc. Pauling introduced the concept of hybridisation.

Hybridisation:

(a) It was introduced by Pauling, to explain equivalent nature of covalent bonds in a molecule.

(b) **Definition** : Mixing of different shapes and approximate equal energy atomic orbitals, and redistribution of energy to form new orbitals, of same shape & same energy. These new orbitals are called hybrid orbitals and the phenomenon is called hybridisation.

(c) Central atom undergoes hybridisation

(d) This process takes place before bond formation

(e) In hybridisation fulfilled, half-filled and empty orbitals can participate

Structure of hybrid orbital

(f) Number of the hybrid orbitals formed is equal to number of atomic orbitals participate in hybridisation.

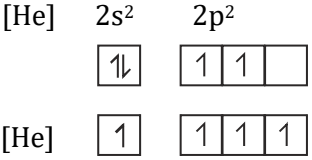
(g) Each hybrid orbital having two lobes, one is major and other is minor. Bond will be formed from major lobe.

(h) The directional properties in hybrid orbital is more than atomic orbitals. Therefore hybrid orbitals form stronger sigma bond.

(i) Hybrid orbital should be arranged in such a way that repulsion between hybrid orbital should be minimum.

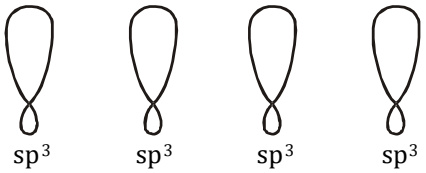
CH_4

C : [He] $2s^2$ $2p^2$

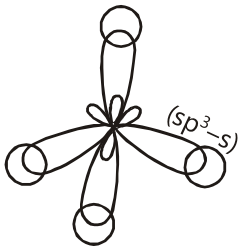


C* : [He]

atomic orbitals



Hybrid orbitals



CH_4 molecule

Determination of hybridisation state:

To predict hybridisation following formula may be used :

Steric Number (S.N.) = Number of σ-bond around that atom + Number of lone pair on that atom.

Molecule	Steric number	Hybridisation
$NH_4^{\oplus}$	S.N. = 4 + 0 = 4	sp^3 hybridisation.
SF_4	S.N. = 4 + 1 = 5	sp^3d hybridisation.
$SO_4^{2\ominus}$	S.N. = 4 + 0 = 4	sp^3 hybridisation.
$NO_3^{\ominus}$	S.N. = 3 + 0 = 3	sp^2 hybridisation.

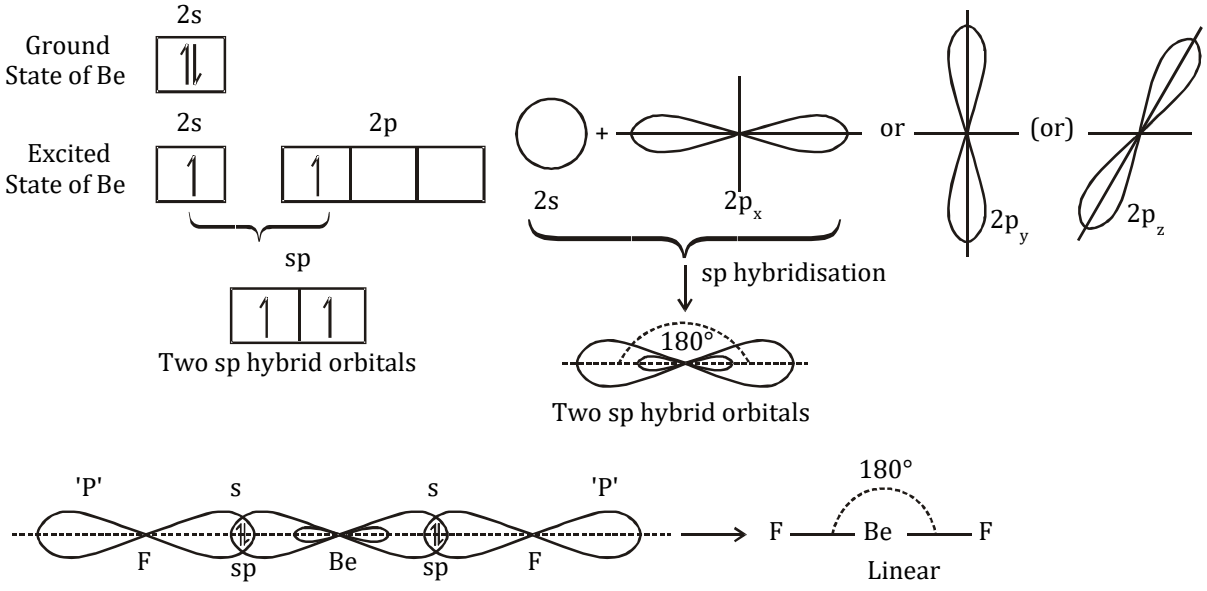
Number of hybrid orbitals	Hybridisation
Two	sp
Three	sp^2
Four	sp^3
Five	sp^3d
Six	sp^3d^2
Seven	sp^3d^3

Types of Hybridisation:

(I) sp hybridisation:

In this type of hybridisation one s-orbital & one p-orbital belong to the same shell of an atom mix together and form two new hybrid orbitals. Which are arrange in straight line at 180° angle.

Example : Formation of BeF_2 molecule :



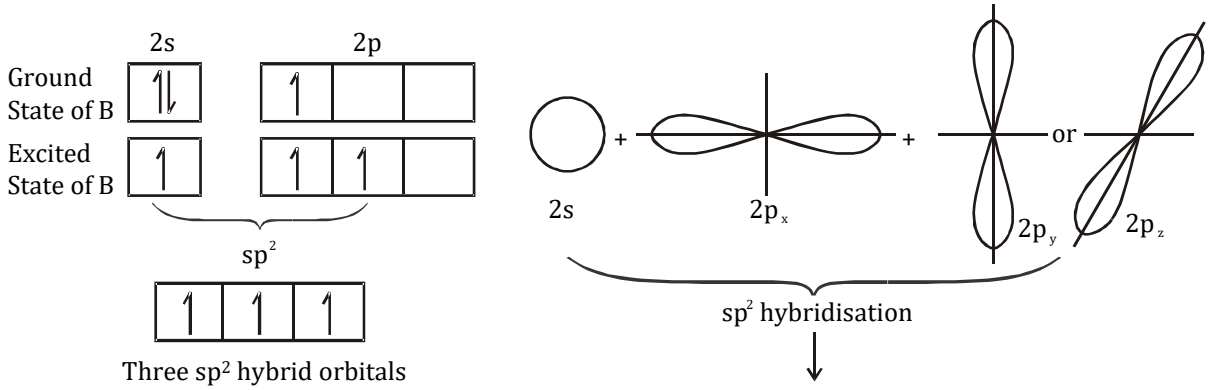
Examples of sp hybridisation

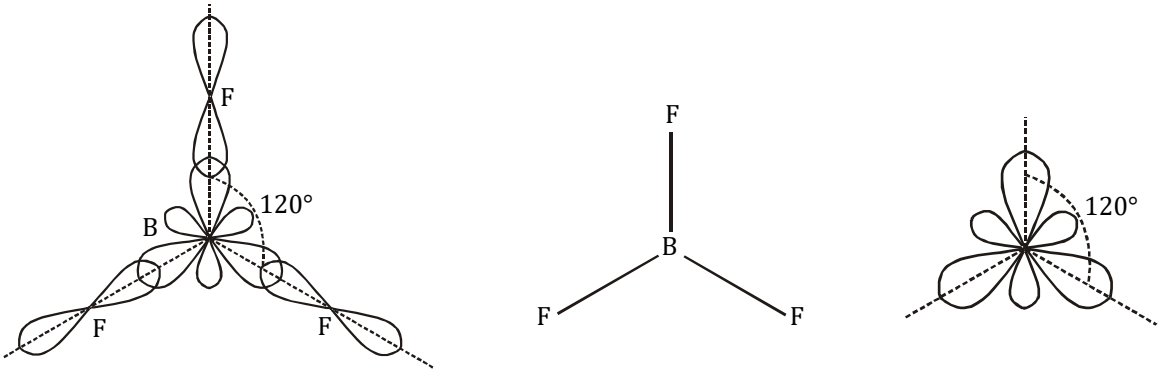
BeH_2, BeF_2, $BeCl_2$, $BeBr_2$, BeI_2, CO_2, CO, $NO_2^{\oplus}$, C_2H_2, HCN, $ZnCl_2$, $HgCl_2$, $CdCl_2$, N_2O, $N_3^{\ominus}$

(II) sp^2 hybridisation:

This type of hybridisation is formed when one s & two p-orbitals belonging to the same shell of an atom mix together and form three new hybrid orbitals. These three sp^2 hybrid orbitals are at angle of 120° & giving trigonal planar shape.

Example : Formation of BF_3 molecule :





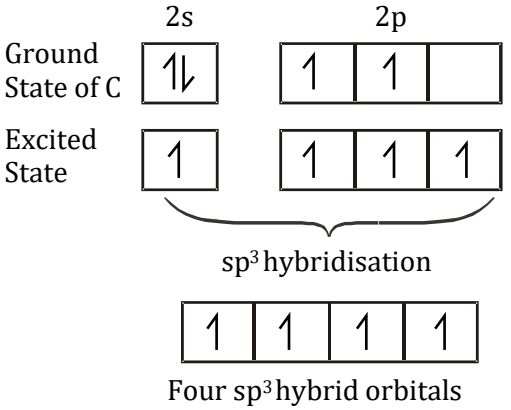
Examples of sp^2 hybridisation

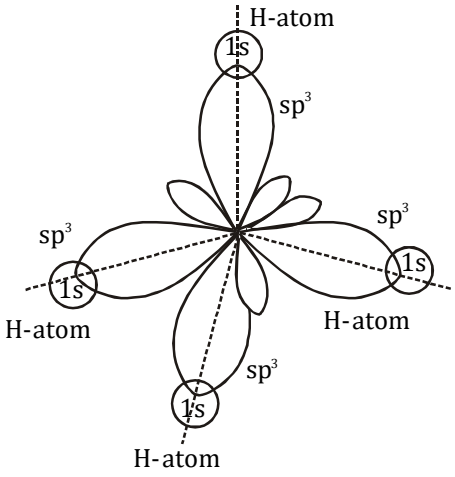
BF_3, BCl_3, $CH_2=CH_2$, Graphite, HNO_3, $NO_3^{\ominus}$, SO_3, $HCO_3^{\ominus}$, $CO_3^{2\ominus}$, $AlCl_3$, $GaCl_3$, $SnCl_2$, $SnBr_2$, SnI_2, $PbCl_2$, HNO_2, SO_2

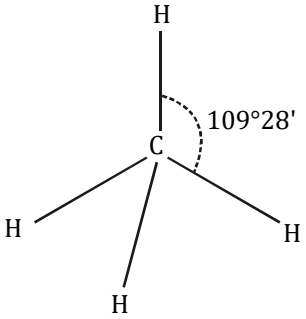
(III) sp^3 Hybridisation:

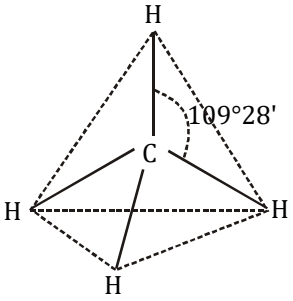
This type of hybridisation is formed when one s & three p-orbital belong to the same shell of an atom mix together & form four new hybrid orbitals. The angle between these four hybrid orbitals will be 109°28'

Example : Formation of Methane molecule :

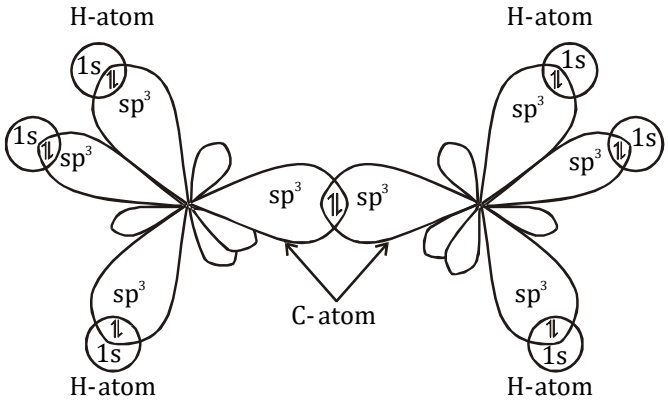


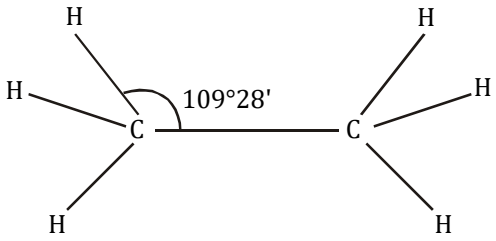






Formation of Ethane molecule:





Examples of sp^3 Hybridisation

CH_4, CCl_4, CBr_4, $PCl_4^{\oplus}$, $NH_4^{\oplus}$, $BF_4^{\ominus}$, $AlF_4^{\ominus}$, $BeF_4^{2\ominus}$, NF_3, NCl_3, $N(CH_3)_3$, PF_3, PCl_3, $AsCl_3$, $SbCl_3$, $BiCl_3$, NH_3, $CH_3^{\ominus}$, $H_3O^{\oplus}$, $SO_3^{2\ominus}$, ClO_3, XeO_3, H_2O, H_2S, $NH_3^{\ominus}$, OF_2, Cl_2O, SCl_2, Diamond, SiO_2, SiC

(IV) sp^3 d Hybridisation:

In this hybridisation one s orbital, three p-orbital and one d orbital (d_{z^2}) are mixed to give five new hybrid orbitals which are equivalent in shape and energy called as sp^3d hybrid orbitals.

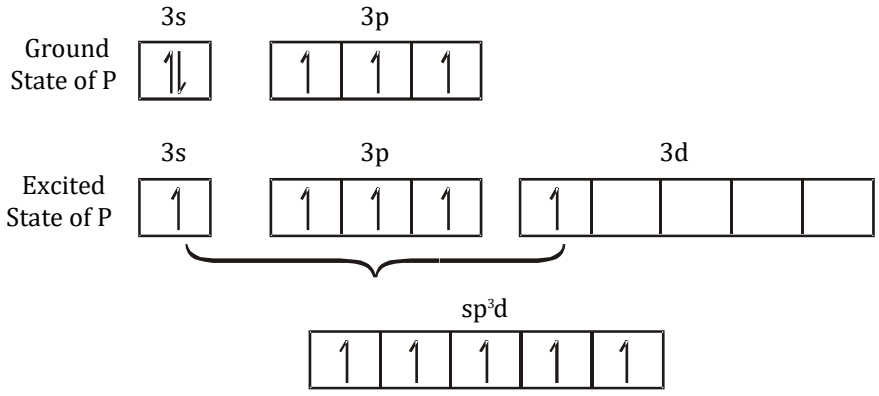
Out of these five orbitals, three hybrid orbitals are at 120° angle and two hybrid orbitals are perpendicular to the plane of three hybrid orbitals that is trigonal planar, the shape of molecule becomes trigonal bipyramidal.

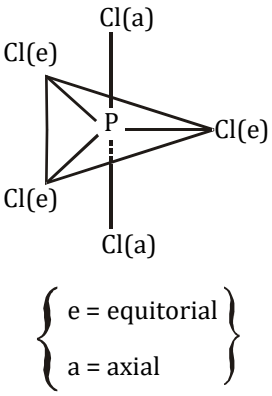
In this way five sp^3d hybrid orbitals form five sigma bond with five Cl atoms and give a molecule of PCl_5, shape of this molecule is trigonal bipyramidal.

Axial(a) two P–Cl bonds are longer than equatorial three P–Cl bond due to repulsion between 3 equatorial(e) bp of $e^{\ominus}$ and 2 axial b.p. of $e^{\ominus}$

In this type of hybridisation one s, three p-orbital and one d-orbital (d_{z^2}) belong to the same shell of an atom mix together & form five hybrid orbitals.

Example : Formation of PCl_5 molecule





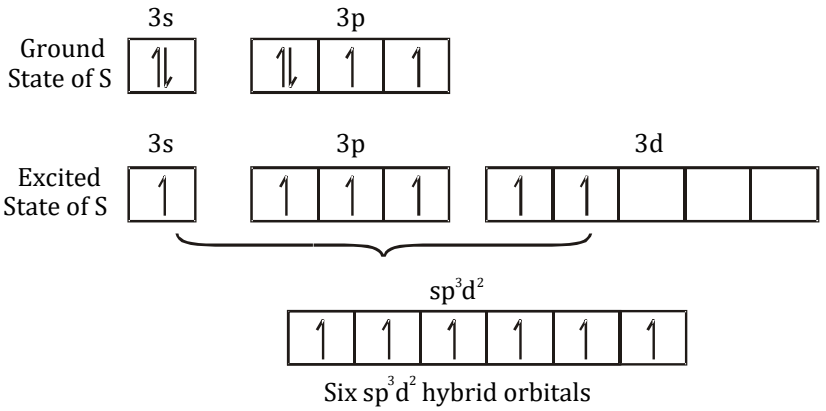
Examples of sp^3d Hybridisation

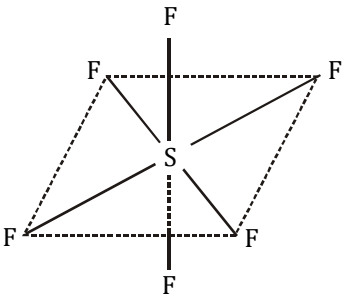
PF_5, PCl_5, PBr_5, AsF_5, $AsCl_5$, $SbCl_5$, SbF_5, SF_4, SeF_4, TeF_4, $PF_4^{\ominus}$, $SbF_4^{\ominus}$, SCl_4, $SeCl_4$, $TeCl_4$, ClF_3, BrF_3, IF_3, $BrCl_3$, ICl_3, $ICl_2^{\ominus}$, $IBr_2^{\ominus}$, $ClF_2^{\ominus}$, $IF_2^{\ominus}$, $BrF_2^{\ominus}$, XeF_2, $I_3^{\ominus}$, $Br_3^{\ominus}$,

(V) sp^3d^2 Hybridisation:

In this type of hybridisation one s orbital, three p-orbitals and two d-orbitals $\left(d_{z^2} \text{ \& } d_{x^2-y^2}\right)$ belong to the same shell of an atom mix together and form six hybrid orbitals. The angle between all hybrid orbitals will be 90°.

Formation of SF_6 molecule :





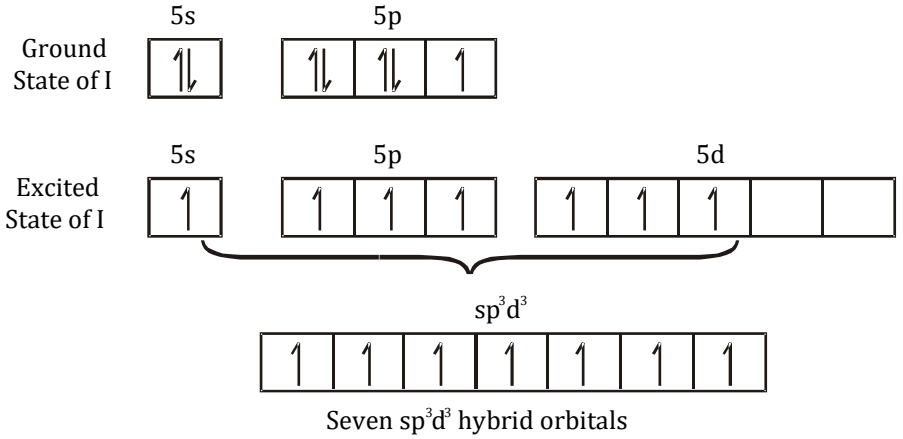
Examples of sp^3d^2 Hybridisation

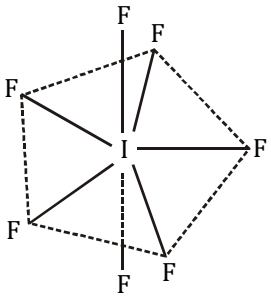
SF_6, $AlF_6^{3\ominus}$, $PF_6^{\ominus}$, ICl_5, $XeOF_4$, ClF_5, $SF_5^{\ominus}$, XeF_4, $ICl_4^{\ominus}$

(VI) sp^3d^3 Hybridisation:

This type of hybridisation is formed when one s orbital, three p-orbitals and three d-orbitals $\left(d_{xy}, d_{z^2}, d_{x^2-y^2}\right)$ belonging to the same shell of an atom mix together & form seven hybrid orbitals. These seven sp^3d^3 orbitals are arranged in pentagonal bipyramidal shape. Five bond angles are of 72° & two bond angles of 90°.

Example : Formation of IF_7 molecule :





Examples of sp^3d^3 Hybridisation

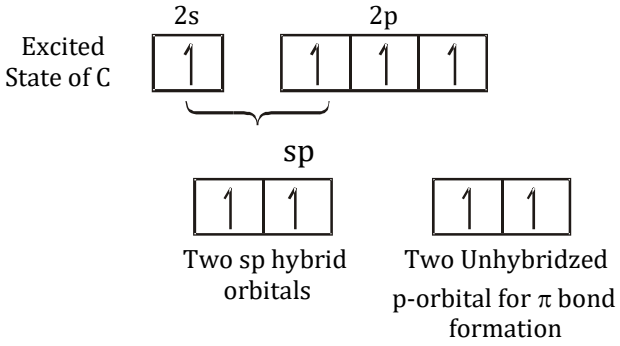
IF_7, XeF_6, $XeF_5^{\ominus}$

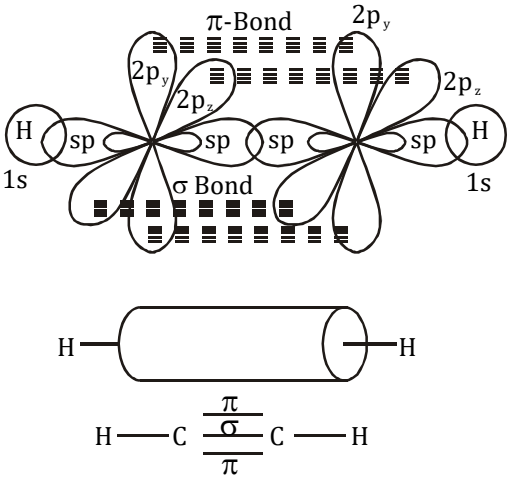
Illustration 1:

Explain the bonding in C_2H_2 and C_2H_4 molecules.

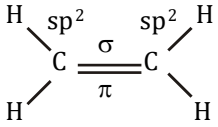
Solution:

Formation of C_2H_2 molecule :

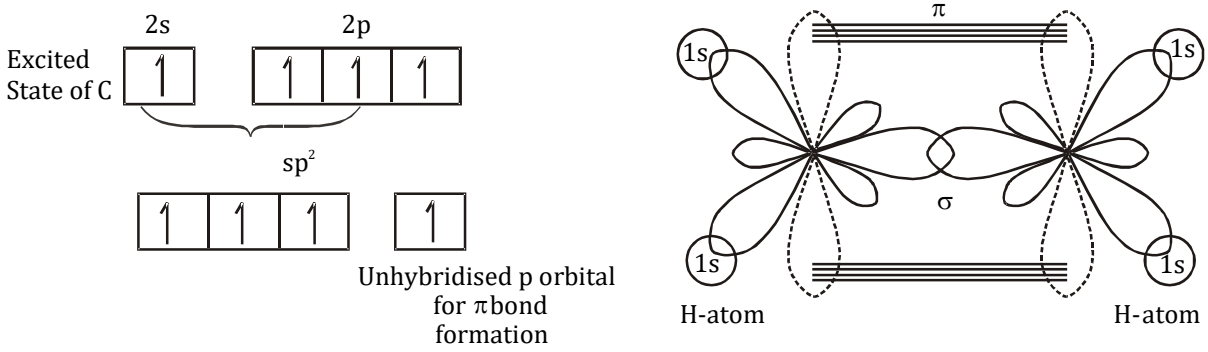


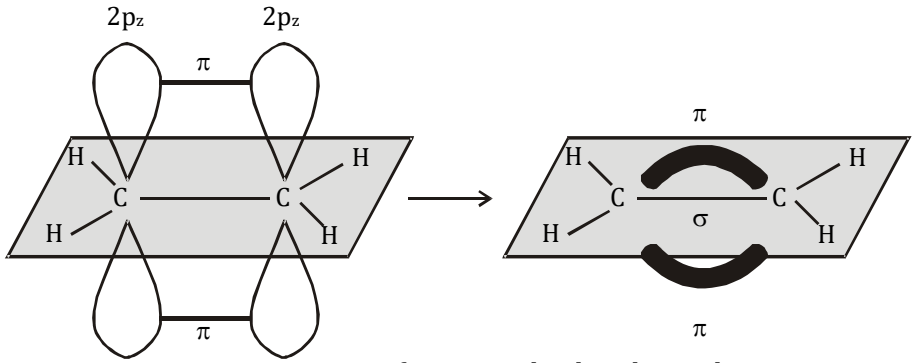


Formation of C_2H_4 molecule :



H–C–H bond angle = 117.6°
H–C–C bond angle = 121°
Bond length (C=C) = 134 pm
Bond length (C–H) = 108 pm





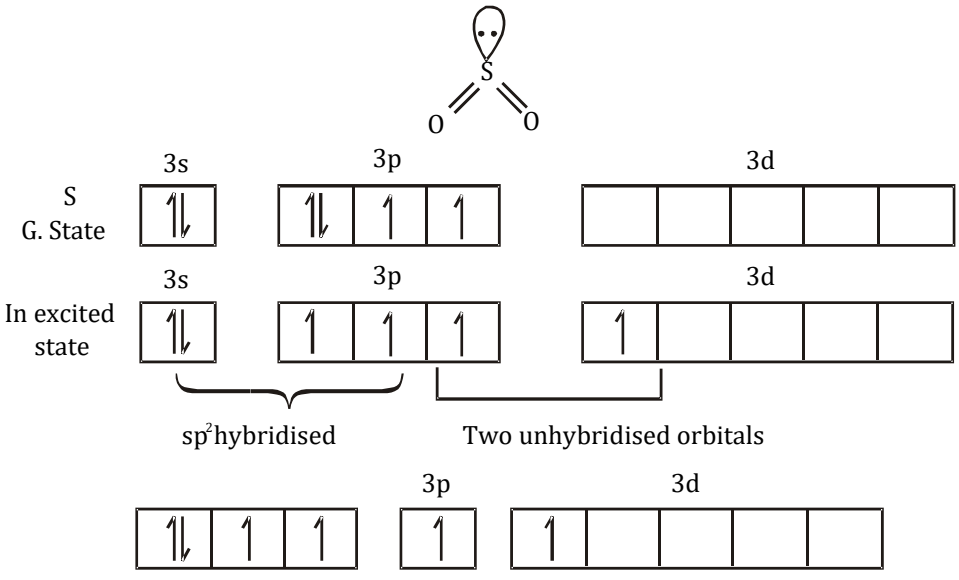
Formation of sigma and pi bonds in ethene

Illustration 2:

Explain the bonding in SO_2 molecules.

Solution:

Formation of SO_2 molecule :



Two π bonds in sulphur are formed by pπ -pπ & pπ– dπ overlapping with p-orbital of oxygen

Atomic orbitals involved in hybridisation:

$s + p_x + p_y + p_z + d_{xy} + d_{yz} + d_{zx} + d_{x^2-y^2} + d_{z^2}$

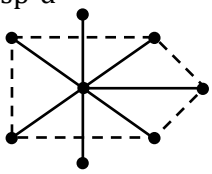
sp	:	s + any p orbital
sp^2	:	s + any two p orbital
sp^3	:	s + all p orbital
sp^3d	:	$s + p_x + p_y + p_z + d_{z^2}$
sp^3d^2	:	$s + p_x + p_y + p_z + d_{z^2} + d_{x^2-y^2}$
sp^3d^3	:	$s + p_x + p_y + p_z + d_{z^2} + d_{x^2-y^2} + d_{xy}$

Illustration 3:

IF_7

Solution:

sp^3d^3



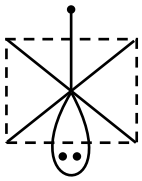
$s + p_x + p_y + d_{x^2-y^2} + d_{xy} + p_z + d_{z^2}$

Illustration 4:

IF_5

Solution:

sp^3d^2



$s + p_x + p_y + d_{x^2-y^2} + p_z + d_{z^2}$

Illustration 5:

ClF_3

Solution:

sp^3d : $s + p_x + p_y + p_z + d_{z^2}$

Illustration 6:

CCl_4

Solution:

$sp^3 : s + p_x + p_y + p_z$

Illustration 7:

SO_2 (in yz plane)

Solution:

$sp^2 : s + p_y + p_z$

Illustration 8:

CO_2 (in z - axis)

Solution:

$sp : s + p_z$

Valence Shell Electron Pair Repulsion (VSEPR) theory:

(a) Molecules having covalent bond have definite geometry as covalent bonding has directional characteristics. A simple theory was given for the molecular shape of the covalent molecules by Gillespie and Nyholm in 1957.

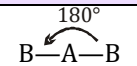
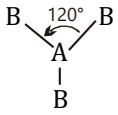
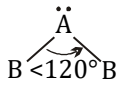
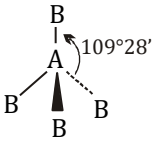
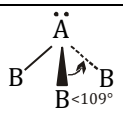
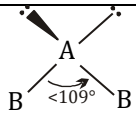
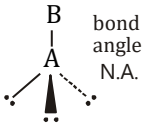
(b) This theory predicts the shape of the molecule by considering the most stable configuration of the bond angles in the molecule. This theory states

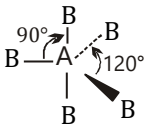
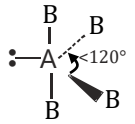
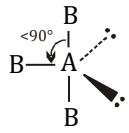
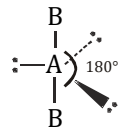
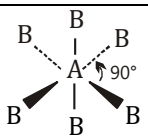
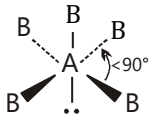
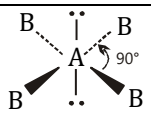
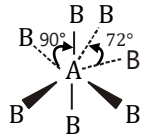
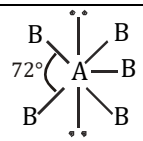
(i) Electron pairs in the valence shell of the central atom of a molecule, whether bonding or lone pairs are regarded as occupying localised orbitals. These orbitals arrange themselves in so as to minimize the mutual electronic repulsions.

(ii) The magnitude of the different types of electronic repulsions follows the order given below:
lone pair-lone pair > lone pair - bond pair > bond pair - bond pair

(iii) The electronic repulsion between two pairs of electrons will be minimum if they are as far apart as possible.
The actual shape of the molecules containing lone pairs is a little distorted from the basic shape as in the NH_3 and H_2O molecules, the bond angles are not 109°28' but 107° and 104.5° respectively due to presence of one lone pair in NH_3 and two lone pairs in H_2O.

Shapes of molecules based on VSEPR theory:

Total no. of hybrid orbitals	No. of b.p. (bond pairs)	No. of unshared pair i.e. *l*p	General formula	Type of hybridisation	Stereo chemical formula/str.	Shape	Exam.
2	2	0	AB_2	sp		linear	$BeCl_2$
3	3	0	AB_3	sp^2		Trigonal planar	BCl_3, $NO_3^{\ominus}$, GaF_3, $CO_3^{2\ominus}$
3	2	1	AB_2	sp^2		V or Bent or angular	$SnCl_2$, O_3, SO_2
4	4	0	AB_4	sp^3		Tetrahedron	CH_4, SiF_4, $\overset{\oplus}{N}H_4$
4	3	1	AB_3	sp^3		Trigonal pyramidal	NH_3, $CH_3^{\ominus}$
4	2	2	AB_2	sp^3		V or Bent or angular	H_2O, SF_2
4	1	3	AB	sp^3		Linear	$ClO^{\ominus}$

5	5	0	AB_5	sp^3d		Trigonal bipyramidal	PF_5, $SF_5^{\oplus}$, $SbBr_5$, XeO_3F_2
5	4	1	AB_4	sp^3d		Seesaw	SF_4
5	3	2	AB_3	sp^3d		T-shaped	ClF_3, BrF_3
5	2	3	AB_2	sp^3d		Linear	$ICl_2^{\ominus}$, XeF_2, $I_3^{\ominus}$
6	6	0	AB_6	sp^3d^2	 All bond∠= 90°	Octahedral or Square bipyramidal	SF_6, $IF_6^{\oplus}$
6	5	1	AB_5	sp^3d^2	 All less than 90°	Square pyramidal	IF_5, $XeOF_4$, BrF_5
6	4	2	AB_4	sp^3d^2		Square planar	$IF_4^{\ominus}$, XeF_4, $ICl_4^{\ominus}$
7	7	0	AB_7	sp^3d^3		Pentagonal bipyramidal	IF_7
7	5	2	AB_5	sp^3d^3		Pentagonal Planar	$XeF_5^{\ominus}$

To identify planarity of molecule, first we predict hybridisation of molecule and draw its shape.

In planar structure all atoms are present in same plane and number of such planer are one.

While in non polar structure first visualise structure in 3d then carefully we check maximum atoms in plane and number of such planes.

Example.

Number of planer SF_6, $CO_3^{2\ominus}$, XeO_3F_2

3 (1) (4)

Bond Parameters:

(A) Bond Angle

(B) Bond Length (Bond distance)

(C) Bond Energy

(A) Bond Angle

The angle between any two adjacent bonds is known as bond angle.

It is represented in degree (°), min (') and second (")

Factors affecting the bond angle -

Step I : Hybridisation or % 's' character : $\boxed{\text{Bond angle} \propto \%\text{ s character}}$

$BeCl_2 > BCl_3 > CCl_4$

180° 120° 109°28'

Step II : Lone pair

When hybridisation is same, lone pair are different.

$$\boxed{\text{Bond angle} \propto \frac{1}{\text{No. of lone pair}}}$$

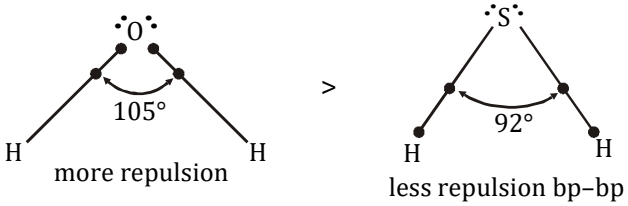
Example :-	**CH_4**		$\ddot{N}H_3$		H_2O
Hybridisation	sp^3		sp^3		sp^3
Bond angle	109°.28'	>	107°	>	104.5°
	(No l.p.)		(one l.p.)		(two l.p.)

- In the different molecules if central atom have same number of lone pair of electron then bond angle will depend on electronegativities of A & B.

Step III : Electronegativity

$\boxed{\text{Bond angle} \propto \text{Electronegativity of central atom}}$

If side atoms are same and EN of central atom increases the bond angle increases.



- Electronegativity of 'O' > Electronegativity of 'S'
- Bond angle of – $NH_3 > PH_3 > AsH_3$

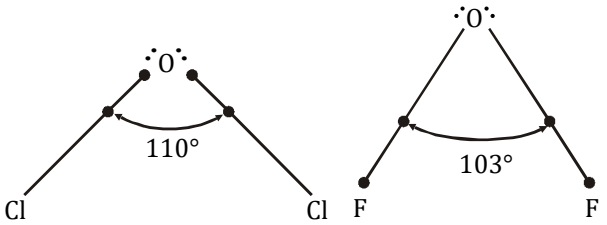
Example :-	$\ddot{N}H_3$	$\ddot{P}H_3$	$\ddot{A}sH_3$
Bond angle	107°	93°	91°

- Electronegativity decreasing.
- Bond angle will decrease

Step IV : Side atom

$$\text{Bond angle} \propto \frac{1}{\text{Electronegativity of bonded atom}} \propto \text{size of side atom}$$

In AB_x type molecules, if central atoms are same and the EN of side atoms increases then bond angle decreases.



Electronegativity of Fluorine is greater than chlorine

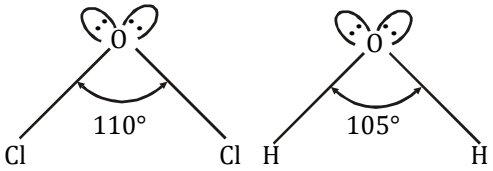
$PF_3 < PCl_3 < PBr_3 < PI_3$ (EN of side atom decrease)

$OF_2 < Cl_2O < Br_2O$

$SF_2 < SCl_2 < SBr_2$

Bond angle depends on size of side atom, On increasing size of side atom bond angle increases.

$Cl_2O > H_2O$



When hybridisation is same, lone pair are same, Central atom is same, bonded atoms are different.

sp^3	OF_2	103 - 105°	Electronegativity
sp^3	Cl_2O	109 - 111°	of bonded atom is
sp^3	Br_2O	116 - 118°	decreasing

(B) Bond Length

The average distance between the nucleus of two atoms is known as bond length, normally it is represented in Å. eg. A ——— B

It depends mainly on electronegativities of constituent atoms.

Case -I. Electronegativity difference is zero then -

Bond length = $r_A + r_B$ or $d_{A-B} = r_A + r_B$

Where r_A is covalent radius of A

r_B is covalent radius of B

x_A is electronegativity of A

x_B is electronegativity of B

If $r_A = r_B$ then Bond length = $2r_A$ or $2r_B$

Example : - Cl – Cl

Case - II Electronegativity difference is not equal to zero then –

Bond length is given by Schomaker and Stevenson formula is - Bond length = $r_A + r_B - 0.09\,(x_A - x_B)$

$x_A - x_B$ = Difference in electronegativities

Factors Affecting Bond Length

(a) Δ electronegativity :-

Bond length $\alpha \frac{1}{\Delta EN}$ {While B.E. $\propto \Delta EN$)

H—F < H—Cl < H—Br < H—I

(b) Bond order or number of bonds :-

Bond length $\alpha \frac{1}{\text{Number of bonds or bond order}}$

ex.	C—C,	C = C,	C ≡ C
Bond length	1.54 Å	1.34 Å	1.20 Å
Bond energy	80	140	180-200 K.Cal.

	C — O	C = O	C ⇇ O
	1.43 Å	1.20 Å	1.13 Å
	—C(—N)<	>C=N—	C ≡ N
	1.47 Å	1.28 Å	1.15 Å

$$\text{Bond length } \alpha \frac{1}{\%s \text{ character}}$$

(C) Bond Energy (BE)

Bond energy may be defined as –

(i) Bond formation energy :- Energy released when any bond is formed is known as bond formation energy or bond energy.

(ii) Bond dissociation energy :- Energy required to dissociate any bond is known as Bond dissociation energy.

Calculation of released energy is more difficult than the dissociation energy therefore dissociation energy of bond is calculated and is assumed as bond energy or bond formation energy.

- **In diatomic molecule :**

  Bond energy = bond dissociation energy

  Example : - $\underset{(N \equiv N)}{N_2} > \underset{(O = O)}{O_2} > \underset{(H - H)}{H_2} > \underset{(F - F)}{F_2}$

Factors Affecting The Bond Energy

(a) Δ Electronegativity (b) Bond order (c) Atomic size (d) Bond polarity
(e) Resonance (f) Hybridisation (g) Lone pair electron

(a) Δ Electronegativity :- Bond energy $\propto \Delta EN$

eg. HF > HCl > HBr > HI

(b) Bond order :- Bond energy $\propto$ Bond order.

eg. C— C < C = C < C ≡ C

79 K. Cal, 143.3 K. Cal., 199.0 K. Cal.

(c) Atomic size :- Bond energy $\propto \frac{1}{\text{Atomic size}}$

Example : $C \equiv C \quad < \quad C \equiv N \quad < \quad N \equiv N$

Exception :- In case of halogen group, order of bond energy is –

$Cl — Cl \quad > \quad Br — Br \quad > \quad F — F \quad > \quad I — I$

Because of higher electron density and small size of F atoms, repulsion between electrons of two F atoms, weakens the bond energy.

Other example S – S > O – O

C – C > Si – Si > Ge – Ge

(d) Bond Polarity :- Bond energy $\propto$ Bond polarity

Example : $H — F \; > \; H — Cl \; > \; H — Br \; > \; H — I$

(e) Resonance :- Bond energy increases due to resonance.

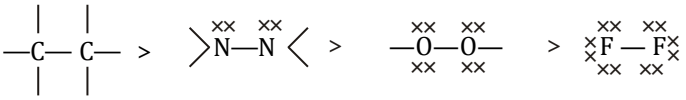
Example : In benzene bond energy of C — C increases due to π electrons of C = C.

(f) Hybridisation :- Bond energy ∝ s-character in hybrid orbitals.

Example : $sp — sp \; > \; sp^2 — sp^2 \; > \; sp^3 — sp^3$

% s character - 50 % 33.3 % 25 %

(g) Lone pair of electrons :- Bond energy $\propto \frac{1}{\text{lone pair of electrons}}$



Size of F and O atoms are small so their bond energy should be high (small atomic radius) but it is actually less, due to lone pair of electrons present on F and O atoms, which repells each other in F—F and —O—O–type of bonds.

Important Note :

(i) Bond strength ∝ overlapping (if orbitals are given)

(ii) Bond strength $\propto \frac{1}{\text{size of orbitals}}$

e.g. 1s – 2p > 1s – 3p > 1s – 4p

(iii) If orbitals are of same shell

Bond strength ∝ extent of overlapping ∝ directional properties

2p – 2p (axial) > 2s – 2p (axial) > 2s – 2s (axial) > 2p – 2p (co-lateral)

(iv) π-bond strength

2pπ – 2pπ > 2pπ – 3dπ > 2pπ – 3pπ > 3pπ – 3pπ

(v) O = O exist but S = S does not exist at room temperature.

(vi) N ≡ N exist but P ≡ P does not exist at room temperature.

(vii) O = C = O exist but O = Si = O does not exist.

Hybridisation of following species in specified state:

Species	Cationic part	Anionic part
PCl_5	$PCl_4^{\oplus}$ (sp^3)	$PCl_6^{\ominus}$ (sp^3d^2)
PBr_5	$PBr_4^{\oplus}$ (sp^3)	$Br^{\ominus}$
XeF_6	$XeF_5^{\oplus}$ (sp^3d^2)	$F^{\ominus}$
N_2O_5	$NO_2^{\oplus}$ (sp)	$NO_3^{\ominus}$ (sp^2)
I_2Cl_6 (liquid)	$ICl_2^{\oplus}$ (sp^3)	$ICl_4^{\ominus}$ (sp^3d^2)
Cl_2O_6	$ClO_2^{\oplus}$ (sp^2)	$ClO_4^{\ominus}$ (sp^3)

Bent's Rule:

(i) A lone pair of electron prefers to occupy that hybrid orbitals which has greater percentage of s-character.

(ii) A more electronegative atom/group prefers to occupy that hybrid orbital which has smaller percentage of s-character.

As s-orbital is more close to nucleus, the electron pair present in s-orbital will experience more attraction of the nucleus, i.e. stability of the system increases, therefore, a lone pair prefers to occupy that hybrid orbital which has greater percentage of s-character.

A more electronegative atom has tendency to attract the shared pair of electron towards itself, thus it will prefer to overlap with that hybrid orbital which has less percentage of s-character (i.e. relatively more distant from nucleus of central atom) because by doing so, it increases the stability of the system.

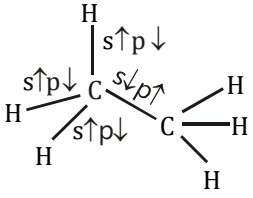
Illustration 9:

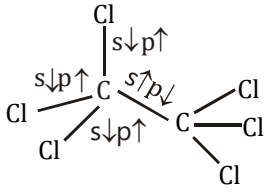
Compare C–C bond length in C_2H_6 and C_2Cl_6

Solution:

In C_2H_6 and C_2Cl_6 both carbon atom are sp^3 hybrid and there is no lone pair of electron on central atom, but all the four sp^3 hybrid orbital around any of the carbon are non-equivalent.

In C_2H_6 molecule, to one of the C-atom three hydrogen atom (less electronegative) and one carbon atom (more electronegative than H) is attached. According to Bent rule, more electronegative carbon will overlap with that hybrid orbital has less character of s-character.





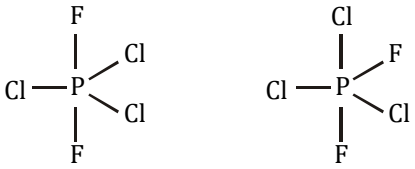
whereas in C_2Cl_6 molecule three Cl-atom (attached to any one of the carbon) will overlap with that hybrid orbital which has less s-character and the other (fourth atom attached with one carbon) being less electronegative will overlap with hybrid orbital which has more s-character. Due to more p-character in C–C bond, bond length in C_2H_6 is more than that in C_2Cl_6.

Hence. C – C(C_2H_6) > C – C(C_2Cl_6)

Illustration 10:

Draw the geometry of PCl_3F_2

Solution:



Correct Structure | Wrong Structure

Because highly electronegative atom occupy axial position (axial position has smaller percentage of s-character).

Drago Generalisation:

On the basis of experimental bond angles of certain molecules fulfilling the following three conditions,

(i) Belongs to third or lower period in periodic table

(ii) Contain atleast one lone pair of electron, and

(iii) Electronegativity of surrounding atom is ≤ 2.5

Drago generalised that in such molecules justification of experimental bond angle can be made satisfactory if one considers no hybridisation, i.e., overlapping of almost pure atomic orbitals.

In such molecules bond angle is approximately 90°.

Group 15	Bond angle	Group 16	Bond angle
NH_3	107°48'	H_2O	104°28'
PH_3	93°36'	H_2S	92°
AsH_3	91°48'	H_2Se	91°
SbH_3	91°18'	H_2Te	90.5°

- Right order of bond angle.

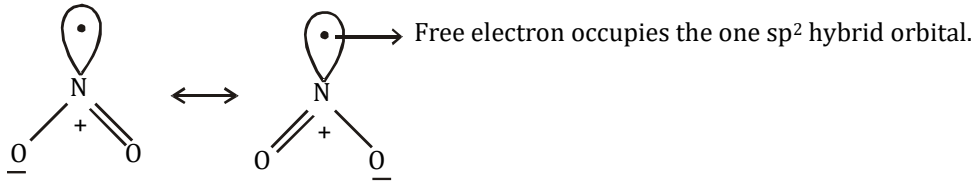
  (a) $H_2O > H_2S > H_2Se > H_2Te$ (b) $NH_3 > PH_3 > AsH_3 > SbH_3$

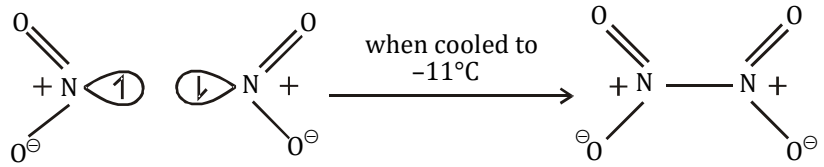
Odd Electronic Species:

(1) NO_2

It is observed that the N–O bond length is in between single bond length and double bond length.

Structure of NO_2 :





Paramagnetic
(unpaired electron)
Brown colour gas

Diamagnetic
(no unpaired electron)
white coloured solid

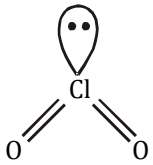
(2) ClO_2

$\Rightarrow \theta = 117°$

$\Rightarrow$ Hybridisation : Approx. sp^2

$\Rightarrow$ Hybrid Orbitals = 3

$Cl : \underbrace{3s + 3p + 3p}_{sp^2 \text{ (}\sigma\text{-bond+l.p)}} + 3p + 3d + \underbrace{3d + 3d + 3d + 3d}_{\text{Unpaired electron is delocalised}}$ ($|\pi$ $|\pi$)



do not form dime

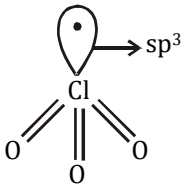
(3) ClO_3

Bond angle = 119°

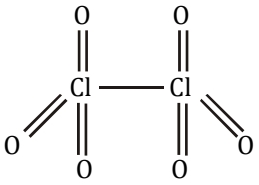
Hybridisation = sp^3

Shape = pyramidal

Structure :



$2ClO_3 \xrightarrow[\text{dimerises}]{\text{readily}} Cl_2O_6$



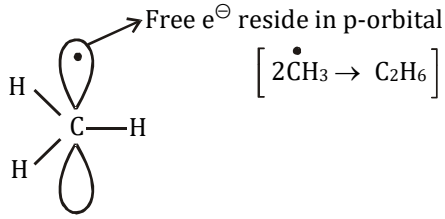
(4) $\dot{C}H_3$

Bond angle = 120°

Hybridisation = sp^2

Shape = planer

Structure :



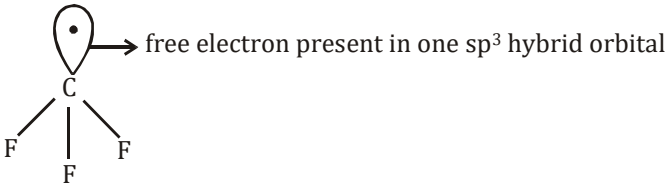
(5) $\dot{C}F_3$

Bond angle = 109°28'

Hybridisation = sp^3

Shape = pyramidal

Structure :



Since the fluorine is more electronegative element which increases the p character in its attached orbital and finally accesses the sp^3 hybridisation hence it is pyramidal in shape.

Molecules that do not exist:

(1) SF_4, SF_6, PF_5 exist while. OF_4, OF_6, NF_5 do not exist

Reason :- Due to the non availability of vacant 2d-orbital, N and O atom can't expand their octet.

(2) (a) PI_5(vap) & SCl_6 do not exist

Reason :- Due to the steric crowding of the surrounding atoms.

(b) SCl_6 does not exist while $TeCl_6$ exist

Reason :- Size of Te > Size of S.

(c) PI_5 (Solid) exist

Reason :-Steric crowding is avoided by the formation of ion pair like $[PI_4]^{\oplus}$ $[I^{\ominus}]$ (Steric crowding is avoided).

(3) SF_6, PF_5, XeF_6, XeF_4, XeF_2 exist while SH_6, PH_5, XeH_6, XeH_4, XeH_2 do not exist

Reason :- F is more electronegative and causes **d-orbital contration** by which the required hybridisation is possible and H is less electronegative, can't do so and the required hybridisation is not possible, hence above compounds do not exist.

Dipole Moment : (Ionic Nature in Covalent Bond)

Due to difference in electronegativity a covalent bond acquires a partial polar character. The two charged ends of the polar bond behave as electric dipoles and degree of polarity is expressed in term of dipole moment.

Dipole moment is defined as the product of the magnitude of charge on any one of the atoms and the distance between them

$\mu = q \times d$

q = charge on any one of the atom which is in the order of 10^{-10} esu or 10^{-19} coloumb and

d = distance between charged atoms is in the order of 10^{-8} cm.

10^{-18} esu cm = 1 debye (unit of dipole moment)

In S.I. system

$$1 \text{ esu} = \frac{1.6\times10^{-19}}{4.8\times10^{-10}} = 3.33 \times 10^{-10} \text{C}$$

$1 \text{ cm} = 10^{-2} \text{ m}$

$1 \text{ D} = 10^{-18} \times 3.33 \times 10^{-10} \times 10^{-2} \text{ cm}$

$1 \text{ D} = 3.33 \times 10^{-30} \text{ cm}$

Note :

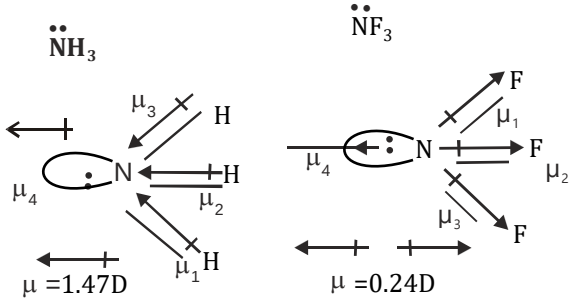
1. Symmetrical molecule without lone pair of electrons has $\mu = 0$. e.g. CO_2, BeF_2, BF_3, CCl_4, etc.
2. Dipole moment is a vector quantity. Therefore individual dipole moments should be added vectorially to get net dipole moment.
3. In a bond H–X, the hydrogen atom is the positive end of dipole where X is an atom more electronegative than H.
4. In a bond C–X, the carbon atom is the positive end of the dipole where X is an atom other than carbon. However, in the C–H bonds of hydrocarbons, the value and directions of the dipole are not constant and depends upon the state of hybridization of the carbon.

   Diatomic molecules will always have dipole moment if it is made of two different atom. Dipole moment further increases with electronegativity differences.

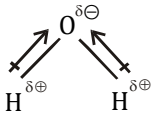
5. The direction of dipole is towards negative centre. It is represented by an arrow pointing from positive centre towards the negative centre
6. The resultant dipole moment depends upon magnitude of bond moments and the angles between the bonds and given by parallelogram law as : ($+\longrightarrow$)
7. **Polyatomic molecules :** A poly atomic molecules is made up of more than two atoms joined by polar covalent bonds and their dipole moment will be the vector sum of dipole moment of different bond & lone pair which depends on spatial orientation of bond.

$\mu_{resultant} = \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2\cos\theta}$

For example :



(XI) Dipole moment of H_2O is 1.85 D which is resultant μ of two O–H bonds.



Application of dipole moment:

(I) To determine polarity and geometry of molecule -

If μ = 0 compound is non-polar and symmetrical

eg. CO_2, BF_3, CCl_4, CH_4. BeF_2 etc.

If μ ≠ 0 compound will be polar and unsymmetrical.

H_2O, SO_2, NH_3, Cl_2O, CH_3Cl, $CHCl_3$ etc.

(II) To calculate % ionic character :-

$$\% \text{ Ionic character} = \frac{\text{Experimental value of } \mu}{\text{Theoritical value of } \mu} \times 100$$

Some important orders of dipole moments-

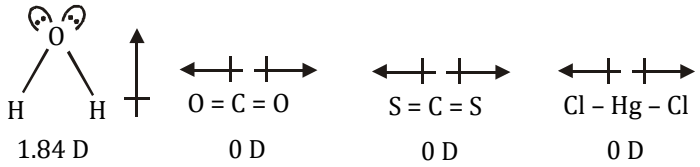
1. (i) $HF > H_2O > NH_3 > NF_3$
   (ii) $CH_3Cl > CH_3F > CH_3Br > CH_3I$
   (iii) $HF > H_2O > SO_2 > NH_3 > PH_3 < PCI_3$
   (iv) $NO_2^{\ominus} > NO_2 > NO_2^{\oplus}$
   (v) $CH_3Cl > CH_2Cl_2 > CHCl_3 > CCl_4$
   (vi) $H_2O > H_2S$
   (vii) $BF_3 < NF_3 < NH_3$
   (viii) $H_2O < H_2O_2$

2. Inorganic substances:

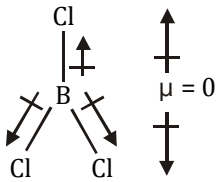
(a) Monoatomic molecules such as He, Ne, etc., have zero dipole moment because they are symmetrical.

(b) Diatomic molecules such as H_2, Cl_2 and N_2 have no dipole moment; so these molecules are symmetrical.

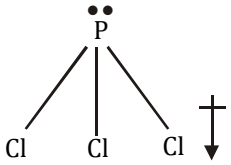
(c) Triatomic molecules some of these molecules possess zero dipole moment so they have a symmetrical linear structure, **Ex.** CO_2, CS_2, $HgCl_2$. Others like water and sulphur dioxide have definite dipole moments. They are said to have angular or bent structures. (V-shaped)



(d) Tetratomic molecules some molecules like BCl_3 have zero dipole moment. They are said to possess a flat and symmetrical (triangular) structure; other example are BF_3, BBr_3, $CO_3^{2\ominus}$, and $NO_3^{\ominus}$

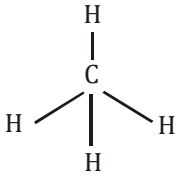


(e) PCl_3, $AsCl_3$, NH_3, PH_3, AsH_3, $H_3O^{\oplus}$ have appreciable dipole moment. They possess trigonal pyramidal structure.



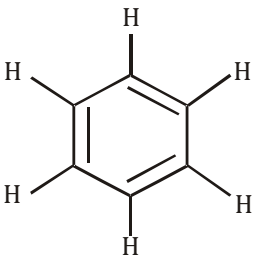
3. Organic substances :

(a) Methane and CCl_4 have zero dipole moment. So they possess symmetrical tetrahedral structures with C atom at the centre of the tetrahedron.

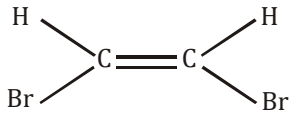


Methane

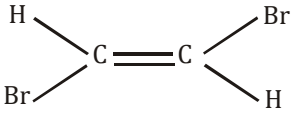
(b) Benzene has zero dipole moment. All the 6C and 6H atoms are assumed to be in the same plane (symmetrical hexagonal structure).



(c) Measurement of dipole moments will enable us to detect cis-and trans isomers of organic compounds (you will learn about cis-trans or geometrical isomerism later in the organic chemistry).
The trans-isomer, which is symmetrical, has zero dipole moment while the cis-isomer has a definite dipole moment.

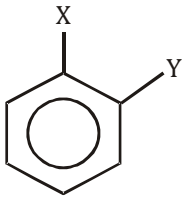


cis-dibromoethylene (μ = 1.4D)

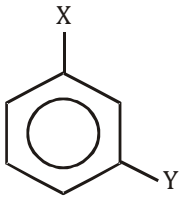


trans-dibromoethylene (μ = 0)

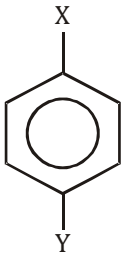
(d) The dipole moments of the aromatic compounds present a very good illustration of dipole moment. We know that when substituted benzene is treated with reagent different products (namely ortho, meta and para products) are formed. The dipole moments of these products are different since the orientation of the groups is different. Let us take an example to clarify it. Let us take three isomers. o-nitrophenol, m-nitrophenol and p-nitrophenol. We also have three other isomers, o-aminophenol, m-aminophenol and p-aminophenol. We want to arrange these isomers in the order of their dipole moments.



Ortho



Meta



Para

In those cases where X = Y, the para isomer becomes symmetrical and have zero dipole moment. In order to find their dipole moment, we need to know about the nature of the groups linked to the benzene ring. In nitro phenols, one group (OH) is electron pushing and the other (NO_2) is electron withdrawing while in aminophenols, both the groups (OH and NH_2) attached are electron pushing. So, depending on the nature of the groups attached, the isomers have different dipole moment.

Hydrogen Bonding:

Definition

(a) It is an electrostatic attractive force between covalently bonded hydrogen atom of one molecule and an electronegative atom (F, O, N & sp hybrid carbon)
(b) It is not formed in ionic compounds.
(c) H–bond forms in polar covalent compounds, (not in non-polar).
(d) It is very weak bond but stronger than vander waal's force.
(e) It is also known as dipole-dipole attraction.

$H^{\delta\oplus}$ — $F^{\delta\ominus}$ ..... $H^{\delta\oplus}$ — $F^{\delta\ominus}$ ..... $H^{\delta\oplus}$ — $F^{\delta\ominus}$

Main condition for H–bonding:

(a) H should be covalently bonded with highly electronegative element like F, O, N.
(b) Atomic size of electro –ve element should be small.

Decreasing order of atomic size is -

N > O > F

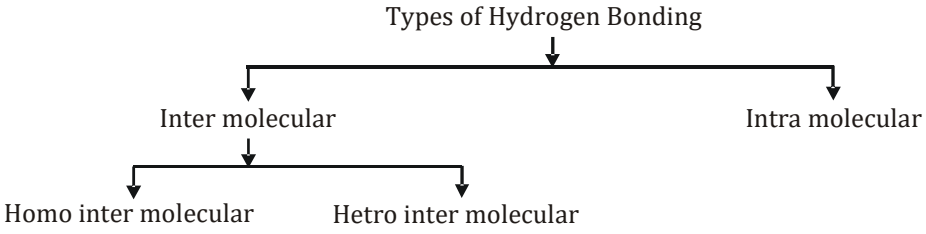
Decreasing order of electronegativity is -

F > O > N
(4.0) (3.5) (3.0)

(c) Strength of H–bond $\propto$ Electronegativity of Z (element) $\alpha \frac{1}{\text{atomic size of Z}}$

(d) Hydrogen bonding occurs in HCN, due to (–C ≡ N) triple bond (sp hybridisation), electronegativities of carbon and nitrogen increases.

H — C ≡ N ..... H — C ≡ N ..... H — C ≡ N



Intermolecular H–Bond:

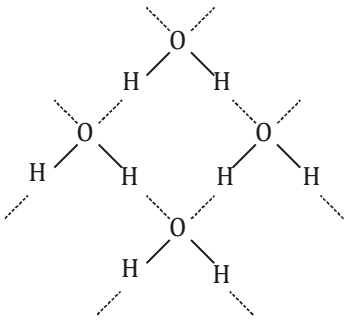
H–bond formation between two or more molecules of either the same or different compounds known as **Inter molecular H-bonding.**

More association takes place in intermolecular H-bonding that's why having more strength.

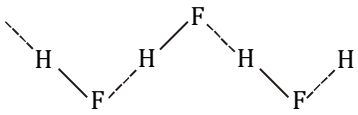
These are of two types :-

(i) Homo intermolecular :- H–bond between molecules of same compounds

eg.

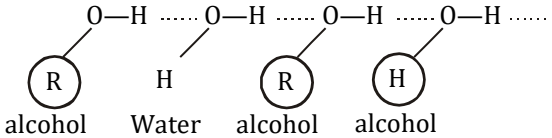


Extent of H-bonding is more because one molecule of H_2O attached with 4 H_2O molecule



Strength of H-bonding is more in HF molecule due the high electron negativity of flourine as compare to oxygen

(ii) Hetro intermolecular :- H–bond between molecules of different compounds



Eg. between alcohol and water

Intramolecular H–bond

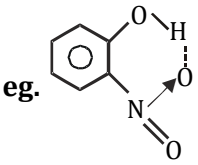
It takes place within the molecule.

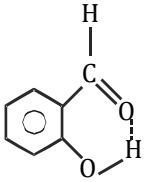
(a) H–bonded with electronegative element of a functional group, form H–bond with another electronegative element present on nearest position on the same molecule.

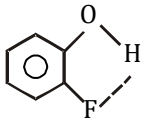
(b) This type of H–bond is mostly occurred in organic compounds.

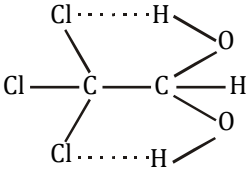
(c) It results in ring formation (Chelation).

(d) Less association in comparison to inter molecular H-bond, so it will have less strength.

eg.  o–nitrophenol

 Salicylaldehyde

 o–fluorophenol

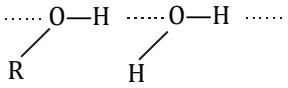
 Chloral hydrate

Effect of H–bond on Physical Properties

(A) Solubility

- **Inter molecular H–bonding**

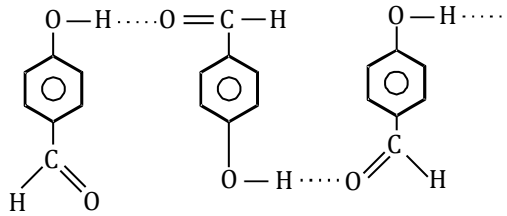
(i) Few organic compounds (Non-polar) are soluble in water (Polar solvent) due to H–bonding.



Other examples - Glucose, Fructose etc. dissolve in water.

(ii) Ketone, ether, alkane etc. are insoluble (no H–bond). Dimethyl ether is soluble in water while diethyl ether is partially soluble, due to bulky ethyl groups H–bonding interrupts.

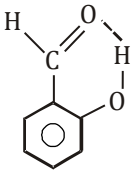
(iii) **Solubility order**-$CH_3OCH_3 < CH_3OH$



p–hydroxy benzaldehyde.

It can form H–bond with water molecule so it can dissolve.

- **Intra molecular H–bonding**



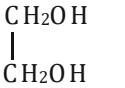
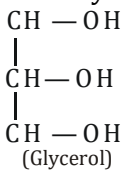
(i) It decreases solubility as it forms chelate by H–bonding, so $H^{\ominus}$ is not free for other molecule.

(ii) It can not form H–bond with water molecule so it can not dissolve.

(B) Viscosity

Viscosity $\propto$ extent of H-bonding $\propto$ – OH groups

H–bond associates molecules together so viscosity increases.

eg. $CH_3OH <$  (Glycol) $<$  (Glycerol)

eg. H_2O (water) $>$ CH_3OH (alcohol) $>$ $CH_3—O—CH_3$ (ether)

eg. $H_3PO_4 > H_2SO_4 > HNO_3$

(C) Surface Tension

Surface tension of a liquid $\propto$ extent of H-bonding.

(D) Melting point and boiling point

(i) Due to intermolecular H–bond M.P. & B.P. of compounds increases.
$H_2O > CH_3OH > CH_3 — O — CH_3$

(ii) Boiling points of VIA, VIIA hydrides are as shown below :
(Group 16 hydrides) **H_2O** > $TeH_2 > SeH_2 > H_2S$
(Group 17 hydrides) **HF** > HI > HBr > HCl

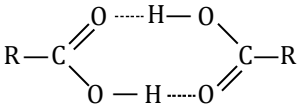
(iii) Sudden increase in boiling point of NH_3, H_2O and HF is due to H–bonding.

(iv) Intramolecular H–bonding gives rise to ring formation, so the force of attraction among these molecules are vander waal force. So M.P. and B.P. are low.
so, o-derivative < p-derivative

(E) Volatility : $\text{Volatility} \propto \frac{1}{\text{H–bonding strength}}$
Intramolecular H-bonding > Intermolecular H-bonding

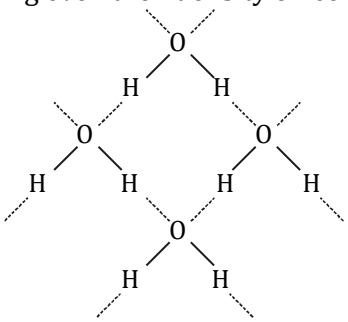
(F) Molecular weight

Molecular wt. of CH_3COOH is double of its molecular formula, due to dimer formation occur by H–bonding.



(G) Physical states

H_2O is liquid while H_2S is gas.
Water and Ice :- Both have H–bonding even then density of ice is less than water.



Volume of ice is more because of open cage like crystal structure, form by association of water molecules with the help of H-bond.
H_2O becomes solid due to four hydrogen bond among water molecule are formed in tetrahedral manner.

Vander Waal's Forces

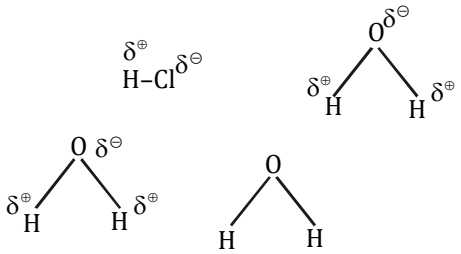
(a) These are the weakest type of inter molecular forces that exist among the molecules which being significant change in physical properties.

(b) These are non-directional, non-valence cohesive forces. These attractive forces being played between the two molecules are independent of the presence of other molecules.

(c) Solid, liquid or gaseous states of many molecules are explained on the basis of inter molecular forces other than covalent, ionic or metallic bonds. Although inert gases do not form any type of bond but may exist in liquid and solid states. This shows that the atoms of inert gases are attracted by each other through some type of inter molecular forces. These intermolecular forces are called **Vander Waal's forces and may be of the following types:**

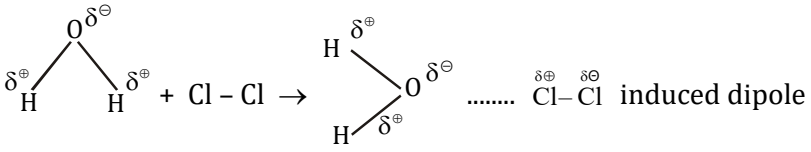
(1) Dipole-dipole attraction :

The force of attraction between the oppositely charged poles of two polar molecules (for example : H_2O, H–F, NH_3 etc.) is called dipole-dipole attraction. This type of attraction is weaker than the ion-dipole attraction.



(2) Dipole-induced dipole attraction :

This type of cohesive forces occurs in a mixture of polar and non polar molecules. The former induce polarity in non polar molecules by disturbing their electron system. for example force of attraction between Cl_2 and H_2O.



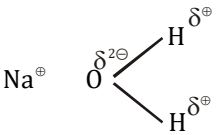
(3) Instantaneous dipole-Induced dipole :

The weak intermolecular forces operating in similar non polar gaseous molecules are called London forces. These forces are very weak in nature and exists only at low temperature. For example weak intermolecular forces in F_2, Cl_2, N_2, molecules and in nobal gasses.

Note : Other weak interactions

(1) Ion-dipole attraction :

Polar molecules are attracted by ions. The negative pole is attracted by cation and positive pole attracted by the anion. This type of attraction is called ion dipole attraction, ion-dipole attraction is observed generally in the process of solvation when sodium chloride ($Na^{\oplus}$ $Cl^{\ominus}$) is dissolved in water because negative poles of water aggregate around $Na^{\oplus}$ ions and positive poles around $Cl^{\ominus}$ ions.



(2) Ion-induced dipole attraction :

When non polar molecules come in contact with ions, its electron cloud gets polarised and the oppositely charged end of it is attracted by the ion. For example attraction between $Na^{\oplus}$ and Cl_2 molecule.

$Na^{\oplus} + Cl - Cl \rightarrow Na^{\oplus}$ ..... $\overset{\delta\ominus}{Cl} - \overset{\delta\oplus}{Cl}$

Factory affecting London dispersion force.
1. Size of Molecule
2. Polarisable Electrons
3. Molecular Mass

Energy distance relationship for the different types of interaction

- Ionic Interaction $E \propto \frac{1}{r}$
- Ion dipole interaction $E \propto \frac{1}{r^2}$
- Dipole – Dipole interaction $E \propto \frac{1}{r^3}$ (for stationary polar molecule)
- Ion – induced dipole interaction $E \propto \frac{1}{r^4}$
- Dipole – induced dipole interaction $E \propto \frac{1}{r^6}$
- Instantaneous dipole – induced dipole interaction $E \propto \frac{1}{r^6}$

Molecular Orbital Theory (MOT)

The molecular orbital theory was developed by F. Hund and R.S. Mulliken in 1932. The salient features are:

(i) Just as electrons of any atom are present in various atomic orbitals, electrons of the molecule are present in various molecular orbitals.

(ii) Molecular orbitals are formed by the combination of atomic orbitals of comparable energies and proper symmetry.

(iii) An electron in an atomic orbital is influenced by one nucleus, while in a molecular orbital it is influenced by two or more nuclei depending upon the number of the atoms in the molecule. **Thus an atomic orbital is monocentric while a molecular orbital is polycentric.**

(iv) The number of molecular orbitals formed is equal to the number of combining atomic orbitals. When two atomic orbitals combine, two molecular orbitals called **bonding molecular orbital** and **anti-bonding molecular orbital** are formed.

(v) The bonding molecular orbital has lower energy and hence greater stability than the corresponding antibonding molecular orbital.

(vi) Just as the electron probability distribution around a nucleus in an atom is given by an atomic orbital, the electron probability distribution around a group of nuclei in a molecule is given by molecular orbital.

(vii) The molecular orbitals like the atomic orbitals are filled in accordance with the **Aufbau principle** obeying the **Pauli Exclusion principle** and the **Hund's Rule of Maximum Multiplicity**.

Formation of Molecular Orbitals : Linear Combination of Atomic Orbitals(LCAO)

According to wave mechanics, the atomic orbitals can be expressed by wave function (ψ), which represent the amplitude of the electron waves. These are obtained from the solution of Shrodinger wave equation.

According to LCAO, the wave function (ψ) of individual atomic orbital linearly combined and form molecular orbitals i.e. during the formation of AB molecule ψ of A and B will linearly combine as $\psi_{MO} = \psi_A \pm \psi_B$

Case I : When two waves are in same phase (constructive interference) the wave adds up and amplitude of new wave is the sum of wave functions of individual atomic orbitals.

$\psi_{MO} = \psi_A + \psi_B$ (Bonding M.O.)

Case II : When two waves are out of phase, the waves are substracted from each other so that the amplitude of new wave is :

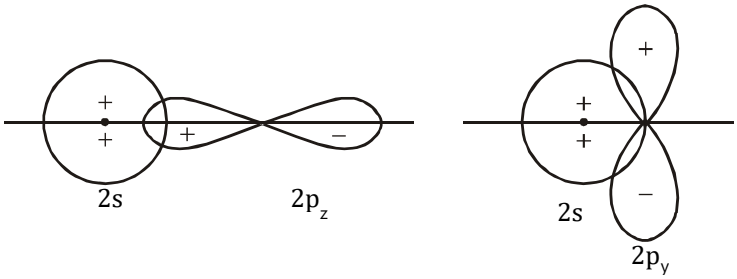
$\psi^*_{MO} = \psi_A - \psi_B$ (Antibonding M.O.)

Conditions for the combination of atomic orbitals:

The linear combination of atomic orbitals to form molecular orbitals takes place only if the following conditions are satisfied :

1. **The combining atomic orbitals must have the same or nearly the same energy.**
   It may be noted that in the homonuclear diatomic molecules of the type A_2 (e.g. H_2, O_2, N_2, F_2 ect.), the participating atomic orbitals must have comparable energies. This means that 1s atomic orbital of one atom can combine with 1s atomic orbital of the other atom and not with its 2s orbital. However, in heteronuclear molecules AB(e.g. HF, HCl etc.) such a combination is permissible

2. **The combining atomic orbitals must have the same symmetry about the molecular axis.** By convention z-axis is taken as the molecular axis. It is important to note that atomic orbitals having same or nearly the same energy will not combine if they do not have the same symmetry. For example, $2p_z$ orbital of one atom can combine with $2p_z$ orbital of the other atom but not with the $2p_x$ or $2p_y$ orbitals because of their different symmetries.



Possible Net overlap = 0

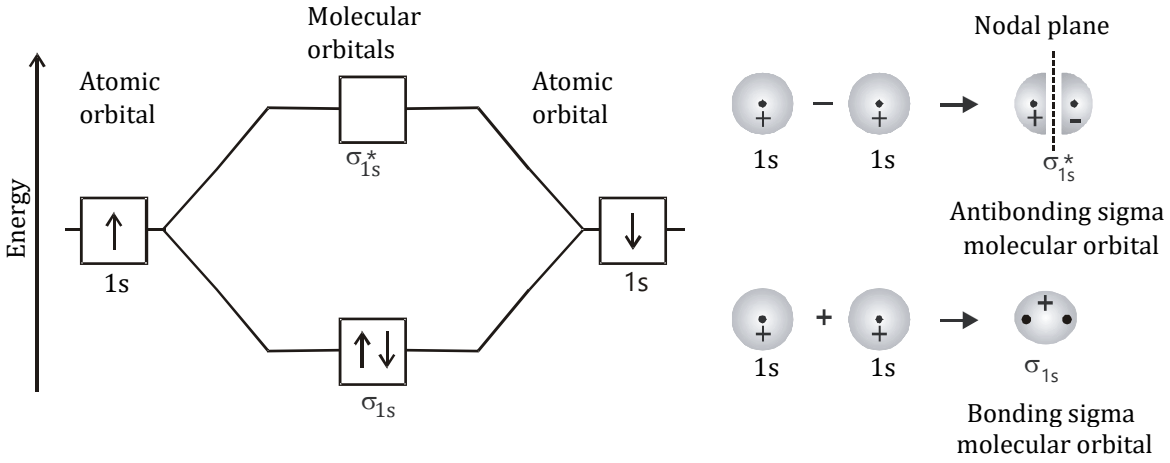
3. **The combining atomic orbitals must overlap to the maximum extent.** Greater the extent of overlap, the greater will be the electron probability density between the nuclei of a molecular orbital.

Types of Molecular Orbitals

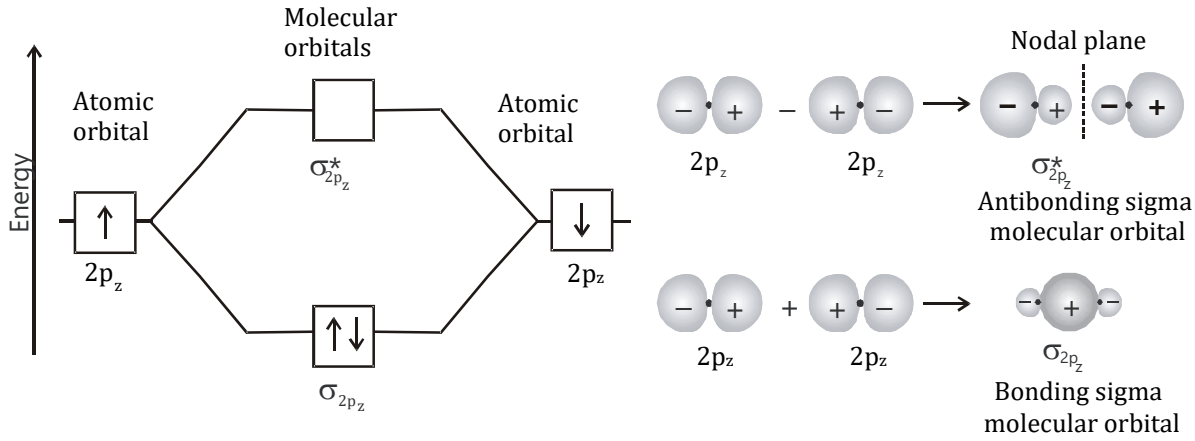
Molecular orbitals of diatomic molecules are designated as σ(sigma), π(pie), δ(delta) etc.

In this nomenclature, the **sigma (σ) molecular orbitals are symmetrical around the inter molecular axis (assume to be z-axis) while pi (π) molecular orbitals are not symmetrical.**

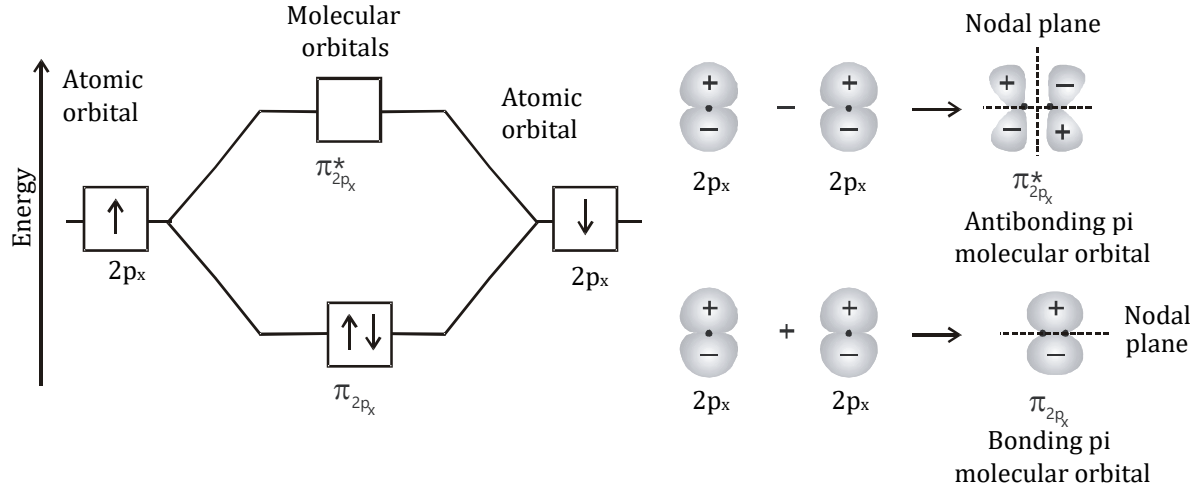
(1) s-s combination of orbitals



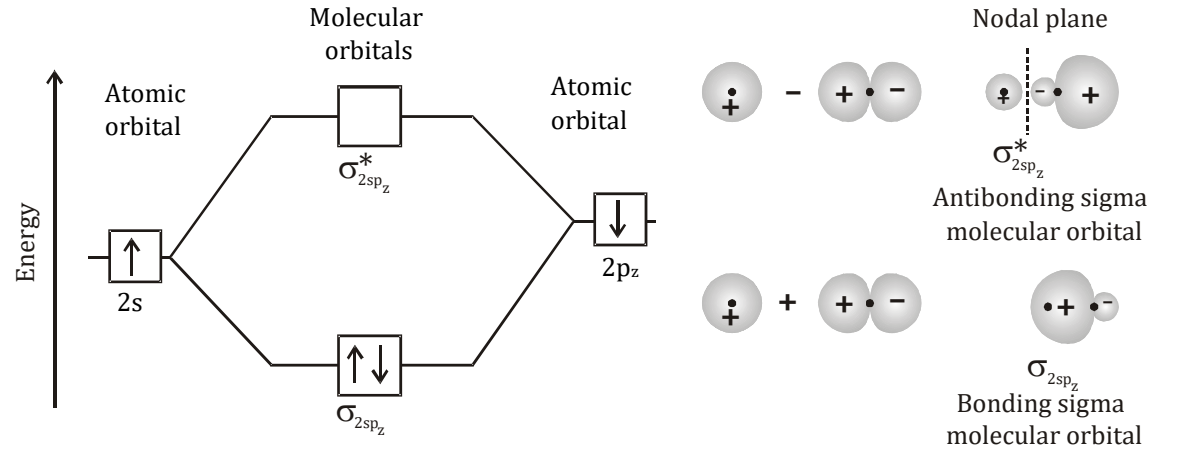
(2)p-p combination of orbitals(end to end overlap)



(3) p-p combination of orbitals (side by side overlap)

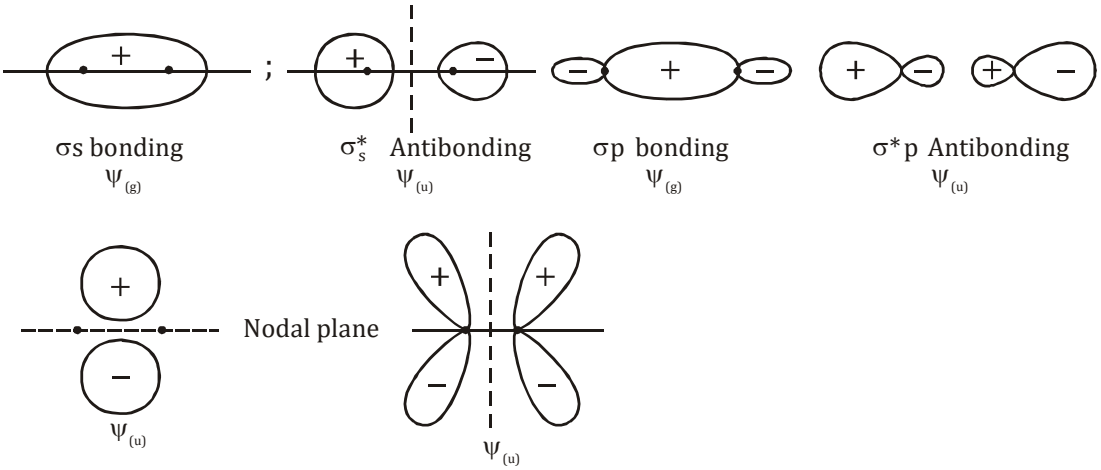


(4) s-p combination of orbitals



Note-1 :

The molecular orbital wave functions are designated as $\psi_{(g)}$ & $\psi_{(u)}$; 'g' stands for gerade (even) and 'u' for ungerade (odd). 'g' & 'u' refers to symmetry of the orbital about its centre. For determining symmetry of the MO is to rotate the orbital about the line joining the two nuclei and then about a line perpendicular to this. If the sign of the lobes remains the same, the orbital is gerade & if the sign changes, the orbital is ungerade.



Note-2 : δ-type of molecular orbitals are obtained by involvement of d-orbitals into bonding.

Energy level diagram from Mos:

Molecular orbital energy diagram for up to N_2 (molecule having ≤ 14 electrons)

$\sigma_{1s} < \sigma^*_{1s} < \sigma_{2s} < \sigma^*_{2s} < \pi_{2px} = \pi_{2py} < \sigma_{2pz} < \pi^*_{2px} = \pi^*_{2py} < \sigma^*_{2pz}$

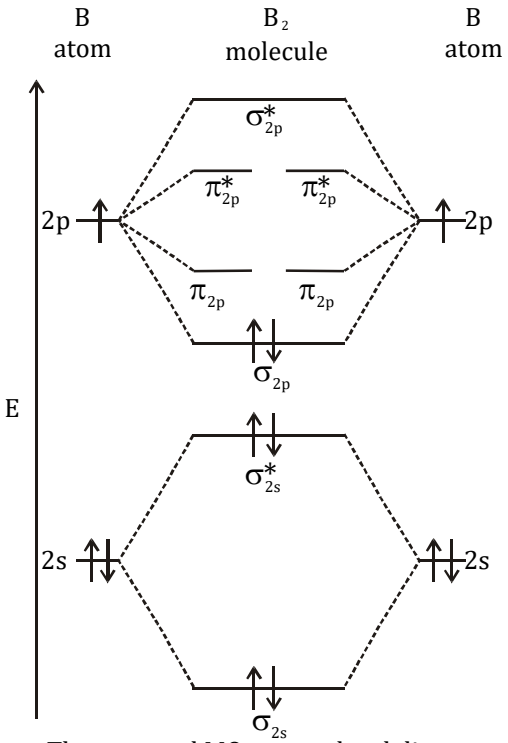
Molecular orbital energy diagram for O_2 and F_2 (molecule having > 14 electrons)

$\sigma_{1s} < \sigma^*_{1s} < \sigma_{2s} < \sigma^*_{2s} < \sigma_{2pz} < \pi_{2px} = \pi_{2py} < \pi^*_{2px} = \pi^*_{2py} < \sigma^*_{2pz}$

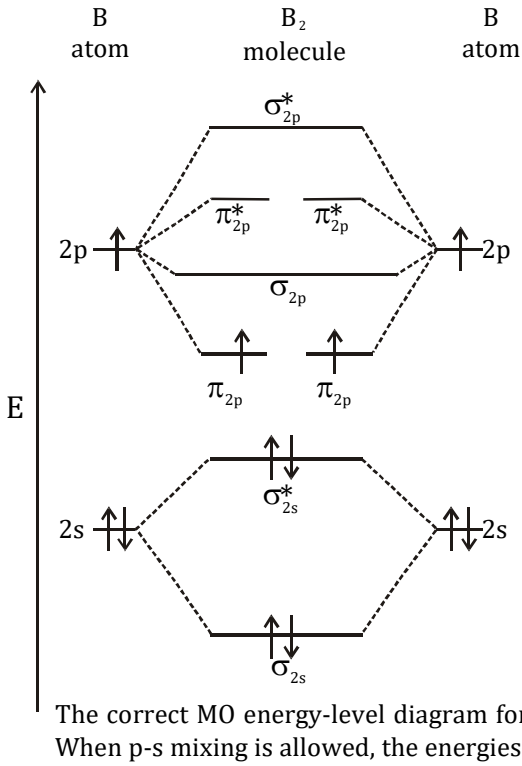
σ *, π * = antibonding molecular orbital

σ, π = bonding molecular orbital

Note : σ_{1s} and σ_{1s}^* molecular orbitals are collectively represented as KK. KK refers to closed K-shell structure.



The expected MO energy-level diagram for the B_2 molecule. According to which B_2 is diamagnetic



The correct MO energy-level diagram for the B_2 molecule. When p-s mixing is allowed, the energies of the σ_{2p} and π_{2p} orbitals are reversed. Therefore, this diagram explains the observed paramagnetism of B_2

sp-mixing :

Rules of Filling up of Molecular Orbital with Electrons :

(1) The molecular orbital with lower energy will be filled first. (Aufbau Principle)
(2) The molecular orbital can accommodate maximum only two electrons. (Pauli's exclusion principle)
(3) If the two MOs have same energy then molecular orbital will first get singly filled and after that pairing will start. (Hunds Rule)

Electronic Configuration And Molecular Behaviour

The distribution of electrons among various molecular orbitals is called the electronic configuration of the molecule. From the electronic configuration of the molecule, it is possible to get important information about the molecule as discussed below.

(i) The molecule is stable if N_b is greater than N_a, and
(ii) The molecule is unstable if N_b is less than N_a

In (i) more bonding orbitals are occupied and so the bonding influence is stronger and a stable molecule results. In (ii) the antibonding influence is stronger and therefore the molecule is unstable.

Where :- N_b is number of electrons in bonding molecular orbitals and N_a is number of electrons in antibonding molecular orbitals.

Bond order:

Bond order (B.O.) is defined as follows Bond order (B.O.) = $\frac{1}{2}$ $(N_b - N_a)$

A positive bond order (i.e., $N_b > N_a$) means a stable molecule while a negative value (i.e., $N_b < N_a$) (i.e., $N_b = N_a$) bond order means an unstable molecule. If bond order zero then molecular does not exist.

Nature Of The Bond

Integral bond order values of 1, 2 or 3 correspond to single, double or triple bonds respectively.

Bond-Length

The bond order between two atoms in a molecule may be taken as an approximate measure of the bond length. The bond length decreases as bond order increases.

Magnetic Nature

If one or more molecular orbitals are singly occupied it is paramagnetic (attracted by magnetic field), e.g., O_2 molecule. Otherwise diamagnetic (eg : N_2)

Molecular Orbital Diagram in Some Homonuclear Diatomic Species

Species	MO Configuration	N_b	N_a	B.O	Magnetic behaviour
H_2	$(\sigma_{1s})^2$	2	0	1	Diamagnetic
He_2	$(\sigma_{1s})^2$ $(\sigma^*_{1s})^2$	2	2	0	_____
Li_2	$(\sigma_{1s})^2$ $(\sigma^*_{1s})^2$ $(\sigma_{2s})^2$	4	2	1	Diamagnetic
Be_2	$(\sigma_{1s})^2$ $(\sigma^*_{1s})^2$ $(\sigma_{2s})^2(\sigma^*_{2s})^2$	4	4	0	_____
B_2	$(\sigma_{1s})^2$ $(\sigma^*_{1s})^2$ $(\sigma_{2s})^2(\sigma^*_{2s})^2$ $(\pi^1_{2px} = \pi^1_{2py})$	6	4	1	Paramagnetic
C_2	$(\sigma_{1s})^2$ $(\sigma^*_{1s})^2$ $(\sigma_{2s})^2(\sigma^*_{2s})^2$ $(\pi^2_{2px} = \pi^2_{2py})$	8	4	2	Diamagnetic
N_2	$(\sigma_{1s})^2$ $(\sigma^*_{1s})^2$ $(\sigma_{2s})^2(\sigma^*_{2s})^2$ $(\pi^2_{2px} = \pi^2_{2py})$ σ^2_{2pz}	10	4	3	Diamagnetic
$N_2^{\oplus}$	$(\sigma_{1s})^2$ $(\sigma^*_{1s})^2$ $(\sigma_{2s})^2(\sigma^*_{2s})^2$ $(\pi^2_{2px} = \pi^2_{2py})$ σ^1_{2pz}	9	4	2.5	Paramagnetic
$N_2^{\ominus}$	$(\sigma_{1s})^2$ $(\sigma^*_{1s})^2$ $(\sigma_{2s})^2(\sigma^*_{2s})^2$ $(\pi^2_{2px} = \pi^2_{2py})$ $\sigma^2_{2pz}\pi^{*1}_{2px}$	10	5	2.5	Paramagnetic
O_2	$(\sigma_{1s})^2$ $(\sigma^*_{1s})^2$ $(\sigma_{2s})^2(\sigma^*_{2s})^2$ σ^2_{2pz} $(\pi^2_{2px} = \pi^2_{2py})$ $(\pi^{*1}_{2px} = \pi^{*1}_{2py})$	10	6	2	Paramagnetic

$O_2^{\oplus}$	$(\sigma_{1s})^2$ $(\sigma^*_{1s})^2$ $(\sigma_{2s})^2(\sigma^*_{2s})^2$ σ^2_{2pz} $(\pi^2_{2px} = \pi^2_{2py})$ π^{*1}_{2px}	10	5	2.5	Paramagnetic
$O_2^{2\oplus}$	$(\sigma_{1s})^2$ $(\sigma^*_{1s})^2$ $(\sigma_{2s})^2(\sigma^*_{2s})^2$ σ^2_{2pz} $(\pi^2_{2px} = \pi^2_{2py})$	10	4	3	Diamagnetic
$O_2^{\ominus}$	$(\sigma_{1s})^2$ $(\sigma^*_{1s})^2$ $(\sigma_{2s})^2(\sigma^*_{2s})^2$ σ^2_{2pz} $(\pi^2_{2px} = \pi^2_{2py})$ $(\pi^{*2}_{2px} = \pi^{*1}_{2py})$	10	7	1.5	Paramagnetic
$O_2^{2\ominus}$	$(\sigma_{1s})^2$ $(\sigma^*_{1s})^2$ $(\sigma_{2s})^2(\sigma^*_{2s})^2$ σ^2_{2pz} $(\pi^2_{2px} = \pi^2_{2py})$ $(\pi^{*2}_{2px} = \pi^{*2}_{2py})$	10	8	1	Diamagnetic
F_2	$(\sigma_{1s})^2$ $(\sigma^*_{1s})^2$ $(\sigma_{2s})^2(\sigma^*_{2s})^2$ σ^2_{2pz} $(\pi^2_{2px} = \pi^2_{2py})$ $(\pi^{*2}_{2px} = \pi^{*2}_{2py})$	10	8	1	Diamagnetic
Ne_2	$(\sigma_{1s})^2$ $(\sigma^*_{1s})^2$ $(\sigma_{2s})^2(\sigma^*_{2s})^2$ σ^2_{2pz} $(\pi^2_{2px} = \pi^2_{2py})$ $(\pi^{*2}_{2px} = \pi^{*2}_{2py})$ σ^{*2}_{2pz}	10	10	0	_____

Colour

Halogens (f_2, Cl_2, Br_2 and I_2) are coloured Reason behind their Colour is HOMO – LUMO transition on moving down the group energy gap between homo-LUMO decreases that's why different halogens shown different colour.

F_2 – yellow

Cl_2 – Greenish yellow

Br_2 – Reddish brown

I_2 – Violet

Ionisation Energy

Ionisation energy of molecule and atom can also be compared by their M.O. diagrams.

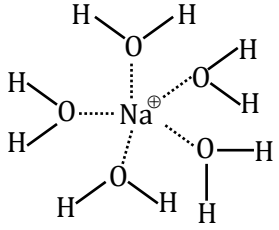
To compare ionisation energy, we compare energy level of HOMO and Atomic orbital of atom. If HOMO having high energy as compere to Atomic orbital then remolsl of electron is easy.

Hydration Energy:

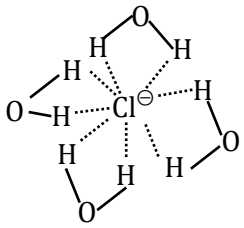
It is the energy released when 1 mol of gaseous ions are hydrated in water. It is directly proportional to nuclear charge and inversely proportional to size. It always decreases down the group.

(a) As the charge density of ion increases hydrated size (or aqueous radius) increases.

Size : $Li^{\oplus}(aq) > Na^{\oplus}(aq) > K^{\oplus}(aq) > Rb^{\oplus}(aq) > Cs^{\oplus}(aq)$



Hydration of $Na^{\oplus}$



Hydration of $Cl^{\ominus}$

(b) As the hydrated size of ion increases ionic mobility decreases, which thus, decreases conductivity of ions.

Mobility : $Li^{\oplus}(aq) < Na^{\oplus}(aq) < K^{\oplus}(aq) < Rb^{\oplus}(aq) < Cs^{\oplus}(aq)$

Conductivity : $Li^{\oplus}(aq) < Na^{\oplus}(aq) < K^{\oplus}(aq) < Rb^{\oplus}(aq) < Cs^{\oplus}(aq)$

(c) Hydration energy also affects the solubility of ionic compounds. If hydration energy is greater than lattice energy then ionic compound will be soluble in water. More is the hydration energy, greater is the solubility, whereas, if lattice energy decreases, solubility of ionic compound increases.

Fajan rule:

Just as all the covalent bonds have some partial ionic character, the ionic bonds also have partial covalent character. The partial covalent character of ionic bonds was discussed by Fajan in terms of the following rules :

- The smaller the size of the cation and the larger the size of the anion, the greater the covalent character of an ionic bond.
- The greater the charge on the cation, the greater the covalent character of the ionic bond.
- For cations of the same size and charge, the one, with electronic configuration $(n-1)d^x ns^0$, typical of transition metals, is more polarising than the one with a noble gas configuration, $ns^2\ np^6$, typical of alkali and alkaline earth metal cations.
- The cation polarises the anion, pulling the electronic charge toward itself and thereby increasing the electronic charge between the two. This is precisely what happens in a covalent bond, i.e., build-up of electron charge density between the nuclei. The polarising power of the cation, the polarisability of the anion and the extent of distortion (polarisation) of anion are the factors, which determine the per cent covalent character of the ionic bond.

$\Rightarrow$ Polarisation power of a cation is usually called ionic potential or charge density.

$$\text{Ionic potential } \phi = \frac{\text{Charge on cation}}{\text{Size of cation}}$$

- **Polarisation Power :**
  The ability of cation to polarise a nearby anion is called polarisation power of cation.

- **Polarizability :**
  (I) It is the ability of anion to get polarised by the cation.
  (II) Polarisation of anion causes some sharing of electron between the ions so ionic bond acquires certain covalent character.
  (III) Increase in polarisation increases covalent character.
  (IV) Magnitude of polarisation depends upon a number of factors, suggested by Fajan and are known as Fajan's rule.

Fajan's rule : (Factors Affecting Polarisation) :

(a) Size of cation :

Polarisation of the anion increases as the size of cation decreases.

In a group –

$BeCl_2$
$MgCl_2$
$CaCl_2$
$SrCl_2$
$BaCl_2$

↓

- Size of cation increases
- Covalent character decreases
- Ionic character increases

Greatest polarising power of $Be^{2\oplus}$, shows its maximum covalent character.

In a period –

$Na^{\oplus}, Mg^{2\oplus}, Al^{3\oplus}, Si^{4\oplus}$ →

- Size of cation decreases
- Covalent character increases

(b) Size of anion :

If the size of the anion increases for a given cation, then covalent character increases.

CaF_2
$CaCl_2$ ↓ - Size of anion increases
$CaBr_2$ - Covalent character increases
CaI_2 - Ionic character decreases

(c) Charge on cation and anion :

Polarisation increases with increase in charge on cation and anion.

(I) Charge on cation and anion ∝ Polarisation (covalent character)

eg.	$NaCl$	$MgCl_2$	$AlCl_3$	$SiCl_4$
	$Na^{\oplus}$	$Mg^{2\oplus}$	$Al^{3\oplus}$	$Si^{4\oplus}$

→

- Charge on cation increases
- Covalent character increases
- Ionic character decreases

(d) Electronic configuration of cation :

Polarisation capacity of cation having pseudo inert gas configuration is high.

$CuCl$ (M.P. 442°C) ⟶ $Cu^{\oplus}$ 2, 8, 18 (Covalent)

$NaCl$ (M.P. 800°C) ⟶ $Na^{\oplus}$ 2, 8 (Ionic)

$Cu^{\oplus}$ and $Na^{\oplus}$ both the cation (Pseudo-inert & inert) have same charge but polarising power of $Cu^{\oplus}$ is more than $Na^{\oplus}$ because –

Z_{eff} of ns^2p^6 (inert) < $Z_{eff.}$ of $ns^2p^6d^{10}$ (pseudo-inert)

$Na^{\oplus}$ < $Cu^{\oplus}$

(Ionic) (Covalent)

So, CuCl has more covalent character than NaCl.

Increased polarisation:

Increased polarisation is responsible for the following changes in the properties of the compounds :

(I) Melting point : The increase of the covalent character is reflected in decreasing melting point of the compounds as illustrated in the following tables. However, other factors may also contribute to the melting point

(II) Solubility in polar solvents : As the covalent character increases, solubility in polar solvents decreases. Thus AgI is much less soluble in water than AgF (or AgCl, or AgBr). Lattice energy consideration alone cannot explain this. Here the solubility decreases from fluoride to iodide due to increasing polarisation of the anion and hence increasing covalent character. The same explanation fits the series $HgF_2 > HgCl_2 > HgBr_2 > HgI_2$ (Solubility in polar solvent).

(III) Electrical conductance in fused state and tendency to ionise in solution : As covalent character increases conductivity in fused state decreases.

Compound	Electrical conductance in fused state ($ohm^{-1}\ cm^2$)	Compound	Electrical conductance in fused state ($ohm^{-1}\ cm^2$)
$LiCl$	166	$NaCl$	133
$BeCl_2$	0.086	$MgCl_2$	29

(IV) Intensity of colour : Polarised anions seem to be responsible for colour in some compounds. As polarisation increases from chloride to iodide, the colour of many metal halides are intensified, as for example :

Colourless	$HgCl_2$	AgCl	$SnCl_4$	$PbCl_2$
Coloured	HgI_2	AgI	SnI_4	PbI_2
	red	yellow	red	Dark yellow

Note : Important thermal stability trends

It is the strength of a compound at high temperatures i.e. a molecule with more thermal stability has more resistance to decomposition at high temperatures.

(1) For compounds having monoatomic anions, thermal stability is decided by the inter-ionic distance. As the inter ionic distance increases lattice energy decreases so thermal stability decreases and its vice versa.

Ex. (a) $Li_3N > Na_3N > K_3N$

(b) $Li_2O > Na_2O > K_2O > Rb_2O > Cs_2O$

(c) $LiX > NaX > KX > RbX > CsX$ (where X = F, Cl, Br, I)

(d) $BeX_2 > MgX_2 > CaX_2 > SrX_2 > BaX_2$ (where X = F, Cl, Br, I)

(e) $Be_3N_2 > Mg_3N_2 > Ca_3N_2 > Sr_3N_2 > Ba_3N_2$

(f) $BeO > MgO > CaO > SrO > BaO$

(2) For the ionic compounds having polyatomic anions, Thermal stability depends on packing of the cations and anions. Larger anions are more stable with larger cations. hence for these anions, thermal stability increases down the group. For example

Ex. (a) $LiClO_3 < NaClO_3 < KClO_3 < RbClO_3 < CsClO_3$

(b) $LiNO_3 < NaNO_3 < KNO_3 < RbNO_3 < CsNO_3$

(c) $LiOH < NaOH < KOH < RbOH < CsOH$

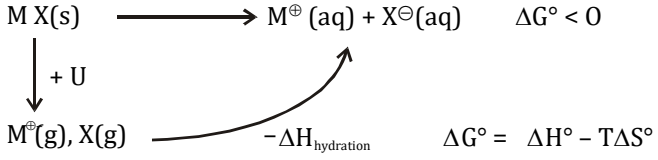
(d) $Li_2CO_3 < Na_2CO_3 < K_2CO_3 < Rb_2CO_3 < Cs_2CO_3$

(e) $Be(OH)_2 < Mg(OH)_2 < Ca(OH)_2 < Sr(OH)_2 < Ba(OH)_2$

(f) Super oxides, peroxides and ozonides of alkali & alkaline earth metals also have the same order.

(e) Solubility :

Ionic compounds are more soluble in polar solvents and less soluble in non polar solvents.



For the solubility of ionic compounds in water, it is necessary that ΔG° must be negative.

Favourable conditions for solubility of ionic compound in water is

$\Delta H_{hydration} > \Delta H_{Lattice\text{-}energy}$

$LE \propto \frac{1}{r^{\oplus} + r^{\ominus}}$, $\quad HE \propto \frac{1}{r^{\oplus} + r^{\ominus}}$

If lattice energy decreases, solubility increases

If hydration energy decreases, solubility decreases

Note : Solubility of ionic compounds in water mainly depends upon hydration energy & lattice energy.

Note : Some important solubility trends of ionic compounds.

(1) In Sulphates of alkaline earth metals solubility decreases down the group
$BeSO_4 > MgSO_4 > CaSO_4 > SrSO_4 > BaSO_4$

(2) In Chlorides of alkaline earth metals solubility decreases down the group
$BeCl_2 > MgCl_2 > CaCl_2 > SrCl_2 > BaCl_2$

(3) In Hydroxides of alkali metals solubility increases down the group
$LiOH < NaOH < KOH < RbOH < CsOH$

(4) In Hydroxides of alkaline earth metals solubility increases down the group
$Be(OH)_2 < Mg(OH)_2 < Ca(OH)_2 < Sr(OH)_2 < Ba(OH)_2$

(5) In carbonates of alkali metals solubility increases down the group
$Li_2CO_3 < Na_2CO_3 < K_2CO_3 < Rb_2CO_3 < Cs_2CO_3$

(6) In $HCO_3^{\ominus}$ of alkaline earth metals solubility increases down the group
$Be(HCO_3)_2 < Mg(HCO_3)_2 < Ca(HCO_3)_2 < Sr(HCO_3)_2 < Ba(HCO_3)_2$

(7) In $F^{\ominus}$ of alkali metals solubility increases down the group
$LiF < NaF < KF < RbF < CsF$

(8) In Oxides of alkaline earth metals solubility increases down the group.
$BeO < MgO < CaO < SrO < BaO$