Chapter 02

Chemical Bonding

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INTRODUCTION

A molecule will be formed if it is more stable and has a lower energy than the individual atom. Normally only electrons in the outermost shell of an atom are involved in forming bonds, and in this process each atom attains a stable electronic configuration of an inert gas.

CHEMICAL BOND

(I) The attractive force which holds various constituents (atoms, ions etc.) together in different chemical species is called chemical bond.

(II) A force that acts between two or more atoms to hold them together as a stable molecule.

(III) It is union of two or more atoms involving redistribution of e^- among them.

(IV) This process accompanied by decrease in energy.

(V) Decrease in energy $\propto$ Strength of the bond.

(VI) Therefore molecules are more stable than atoms.

(VII) In the formation of a molecule, only the outer shell electrons take part in chemical combination and they are known as valence electrons.

Types of Bonds

	Atoms involved	Bonding
(I)	Metal + Nonmetal	Ionic Bond
(II)	Nonmetal + Nonmetal	Covalent Bond
(III)	Metal + Metal	Metallic Bond
(IV)	Electron deficient molecule or ion (Lewis acid) and electron rich molecule or ion (Lewis base)	Coordinate bond
(V)	H and electronegative elements (N, O, F some times with Cl)	Hydrogen – Hydrogen bond

1. Tendency to acquire minimum energy :

(I) When two atoms approaches to each other. Nucleus of one atom attracts the electron of another atom.

(II) Two nuclei and electron of both the atoms repels each other.

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

(IV) **So Attraction $\propto$ 1/energy $\propto$ Stability.**

(V) Bond formation is an exothermic process

2. Tendency to acquire noble gas configuration (octet rule or ns^2, np^6 and $1s^2$) :

(I) Atom combines to acquire noble gas configuration.

(II) Only outermost electron i.e. ns, np and (n-1)d electrons participate in bond formation.

(III) Inert gas elements do not participate, as they have stable electronic configuration and hence minimum energy. (Stable configuration $1s^2$ or ns^2np^6)

Example: When two atoms combine to form a molecule -

(1) Energy is released

(2) Energy is absorbed

(3) Energy is neither released nor absorbed

(4) Energy may either released or absorbed

Solution: **(1)**

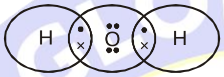
To attain stability energy is released.

(I) Every atom has a tendency to complete its octet outermost.

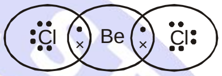
(II) H has the tendency to complete its duplet.

(III) To acquire inert gas configuration atoms loose or gain electron or share electron.

(IV) The tendency of atoms to achieve eight electrons in their outer most shell is known as Lewis octet rule.



Obeys octet rule



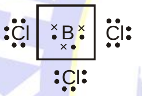
Doesn't obeys octet rule

Limitation of Octet Rule :

(a) Incomplete octet molecules : - or (electron deficient molecules)/ Hypervalent molecules

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

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



In BCl_3

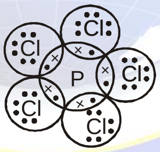
Boron has only 6 electrons

Other examples - $BeCl_2$ $(4e^-)$, $ZnCl_2(4e^-)$, $Ga(CH_3)_3$ $(6e^-)$

(b) Expansion of octet or (electron efficient molecules)/ Hypervalent molecules

Compound in which central atom has more than $8e^-$ in outermost orbits.

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



Electron dot formula of PCl_5

(c) Pseudo Inert gas configuration : -

Pb^{+4} etc. $ns^2np^6nd^{10} \rightarrow$ Pseudo inert gas configuration

$ns^2np^6 \rightarrow$ Inert gas configuration (except He)

Cations of transition metals, which contains 18 electrons in outermost orbit

Examples : Ga^{+3}, Cu^+, Ag^+, Zn^{+2}, Cd^{+2}, Sn^{+4},

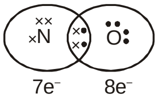
Electronic configuration of Ga - $1s^2$, $2s^22p^6$, $3s^23p^63d^{10}$, $4s^24p^1$

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

(d) Odd electron molecules : -

Central atom have an unpaired electron or odd no $(7e^-, 11e^-$ etc) of electrons in their outer most shell.

Examples : NO, NO_2 ClO_2 etc.



Example: Which follows octet rule -

(1) $FeCl_2$ (2) AgCl (3) $CaCl_2$ (4) CuCl

Solution: **(3)**

Because in other compounds there is more than 8 e^- in outermost shell of central atom.

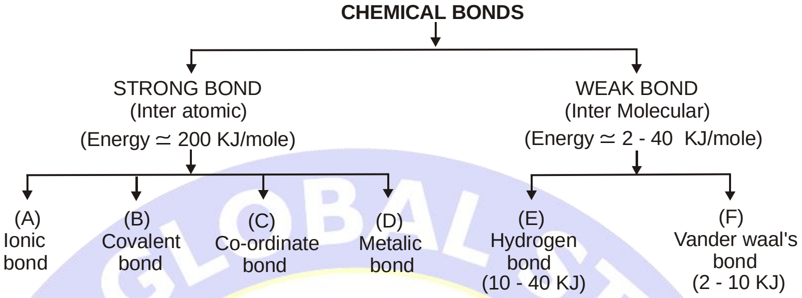
Example: The octet rule is not obeyed in -

(1) CO_2 (2) BCl_3 (3) PCl_5 (4) SiF_4

Solution: **(2) & (3)**

As B is electron deficient, P undergoes octet expansion.

Classification of bonds : -



IONIC, COVALENT AND COORDINATE BONDING

- **Ionic bonding (Electrovalent bonding)**

  An ionic bond is formed when a metal atom transfers one or more electrons to a non-metal atom.

$$\overset{\overset{e^-}{\frown}}{Na \; + \; \tfrac{1}{2}F_2} \longrightarrow Na^+ \Leftarrow\!\!\Rightarrow F^-$$

  The oppositely charged ions get attracted through electrostatic force of attraction.

- **Properties of ionic compounds :**

➢ In the solid state, each cation surrounds itself with anions and each anion with cations. These very large number of ions are arranged in an ordinary network called ionic crystals.

➢ They are good conductors of electricity in fused state or in aqueous solution.

➢ They are generally soluble in polar solvents and insoluble in non-polar solvents.

➢ Have high melting point and boiling point than covalent compounds.

➢ Have strong force of attraction between cation and anion (Coulombic force)

$$F = \frac{KZ_1Z_2e^2}{r^2}$$

Where Z_1 and Z_2 are charge on the ions, $K(4\pi \in_0)$ is dielectric constant of the medium and r the inner-ionic distance (i.e., bond length).

➢ In general ionic bonds will be formed more easily between elements with comparatively low ionization enthalpies and elements with comparatively high negative value of electron gain enthalpy.

Conditions for Forming Ionic Bonds :

Formation of Ionic bond depends upon these three factors –

(a) Ionisation energy :

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.

$$\left.\begin{array}{l} \text{e.g } Na^+ > Mg^{+2} > Al^{+3} \\ \quad Cs^+ > Rb^+ > K^+ > Na^+ > Li^+ \end{array}\right\} \text{Cation formation tendency}$$

(b) Electron affinity

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

Higher electron affinity → Greater tendency to form anion
e.g. Cl > F > Br > I
F > O > N

(c) Lattice energy –

(Energy released) Amount of energy released when one mole of crystal lattice is formed Higher lattice energy → Greater will be the stability or strength of ionic compound.

Factors affecting lattice energy :

(I) Size of ion :

(a) Keeping size of cation constant, the lattice energy decreases with the increases of anionic radius. Hence order of solubility of LiX in water is LiF < LiCl < LiBr < LiI

As solubility $\propto \dfrac{1}{\text{lattice energy}}$

(b) In LiI covalent nature is more according to Fajan's rule but HE > LE therefore Li is more soluble in water.

(c) Keeping size of anion constant, the hydration energy decreases with the increase of cationic radius. hence order of solubility of MSO_4 will be –

$BeSO_4 > MgSO_4 > CaSO_4 > SrSO_4 > BaSO_4$ (Exception of Fajan's rule)

(d) If size of cation and anion is very large, solubility decreases from top to bottom.

(e) Solubility decreases in a period (as ionic nature decreases and covalent nature increases)

$NaCl > MgCl_2 > AlCl_3$

(II) Polarisation of anion :

Polarisation capacity is maximum in pseudo inert gas configuration.

$$\boxed{\text{Solubility} \propto \dfrac{1}{\text{Polarisation}}}$$

AgF > AgCl > AgBr > AgI

$\longrightarrow$

- Polarisation increases.
- Covalent character increases.
- Solubility decreases.

(III) Magnitude of charge → $U \propto z^+ z^-$ (Ionic charge)

Lattice energy ∝ Magnitude of charge

NaCl	$MgCl_2$	$AlCl_3$
Na^+	Mg^{+2}	Al^+

$\longrightarrow$

– Lattice energy increases
– Size of cation decreases.

(IV) Size of Cation : – Lattice energy

LiCl NaCl KCl RbCl CsCl

$\longrightarrow$

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

(d) Overall lowering of energy :

Energy must be released during bond formation.

Energy changes are involved in the following steps –

$A + IE = A^+ + e^-$

and $B + e^- = B^- + EA$

This concludes that for lower value of IE and higher value of EA there is more ease of formation of the cation & anion respectively and consequently more chances of electrovalent bond formation.

Representation of formula of compounds :

(a) 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^+B^-

(b) Write their electrovalencies in figure at the top of each symbol as A^xB^y

(c) Now apply criss cross rule

$$\begin{tikzcd} \text{Valency} & X \arrow[dr] & Y \arrow[dl] \\ \text{Element} & A & B \end{tikzcd}$$

, i.e formula AyBx.

Examples : Calcium chloride

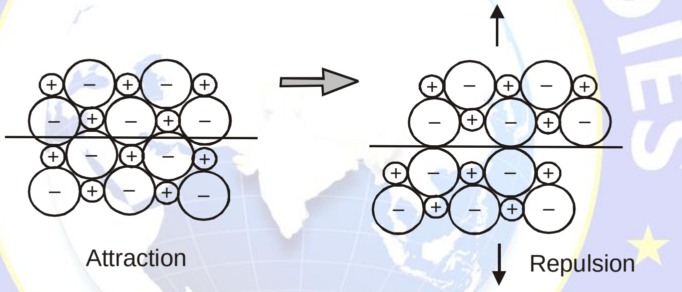
$$\begin{tikzcd} 2 \arrow[dr] & 1 \arrow[dl] \\ \text{Ca} & \text{Cl} \end{tikzcd} = CaCl_2$$

Properties of ionic compounds :

(a) Physical state –

Ionic compounds are hard, crystalline and brittle due to strong electrostatic force of attraction.

Brittleness →



(Same charged ions comes nearer. So they repell each other)

(b) Isomorphism –

(I) Two compounds are said to be isomorphous if they have similar no. of electrons i.e. similar configuration of their cation and anion.

(II) They have similar crystal structure.

Example –

	Na^+	F^-	Mg^{+2}	O^{-2}
Valency	+ 1,	–1	+ 2,	– 2
electronic configuration	2, 8,	2, 8	2, 8	2, 8
similarly	Ca^{+2}	$2Cl^{-1}$	$2K^{+1}$	S^{-2}
	2, 8, 8	2, 8, 8 2, 8, 8	2, 8, 8 2, 8, 8	2, 8, 8

(c) Boiling point and melting point –

Ionic compounds have high boiling point and melting point due to strong electrostatics force of attraction among oppositely charged ions.

(d) Conductivity –

It depends on ionic mobility. In solid state - No free ions - Bad conductor of electricity.

In fused state or aqueous solution Due to free ions - Good conductor of electricity.

conductivity order : Solid state > Fused state < Aqueous solution

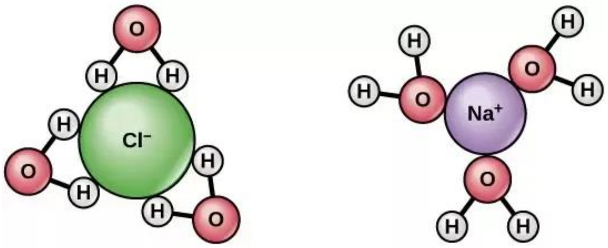
(e) Solubility –

Highly soluble in water (Polar solvents)

Example : NaCl in water

(I) The Na^+ ions get associates with negatively charged 'O' of water

(II) And Cl^- ions associates with positively charged 'H' of water.



(III) Thus charge on Na^+ and Cl^- decreases and electrostatics force of attraction also decreases which leads to free ion.

(IV) The energy released due to interaction between solvent and solute is called solvation energy. If water is used as solvent it is called hydration energy.

(V) For an ionic compound to be soluble in water – Hydration energy > Lattice energy

$$\boxed{\text{Lattice energy} \propto \frac{1}{\text{Solubility}}}$$

Hydration energy $\propto$ Solubility.

Hydration energy (H) $\propto \frac{1}{r^+} + \frac{1}{r^-}$ {r^+ & r^- are radius of cation and anion}

(VI) Hydration energy mainly depends on the cation radius because the value $\frac{1}{r^-}$ is negligible in comparison to $\frac{1}{r^+}$.

(VII) Down the group both the lattice energy & hydration energy decreases, if decreases in lattice energy is greater than hydration energy, solubility increases down the group and vice versa.

Example: Out of following which has maximum value of lattice energy -

(1) NaF (2) NaCl (3) NaBr (4) NaI

Solution: **(1)**

Due to small size of anion.

Example: The crystal lattice of electrovalent compound is composed of -

(1) Atoms (2) Molecules

(3) Oppositely charged ions (4) Both molecules and ions

Solution: **(3)**

It is the fact that electrovalent compounds are made of ions.

Example: Ions are formed from neutral atoms by -

(1) Loss of electron (2) Gain of electrons

(3) Sharing of electrons (4) Loss or gain of electrons

Solution: **(4)**

Cation and anion are formed by losing and sharing of electrons respectively.

Factor affecting solubility :

(I) Dielectric constant –

The **capacity of solvent to neutralise the charge of ionic compounds** is called Dielectric constant.

It is represented by "ε"

(a) Water has maximum dielectric constant (ε = 80)

(CH_3OH ε = 35), (Acetone ε = 21)
(C_2H_5OH ε = 27), (Ether = 4.1)
(Benzene ε = 2.3)
$H_2O > CH_3OH > CH_3CH_2OH > CH_3COCH_3 > CH_3OCH_3 > C_6H_6$

(b) Ionic compounds are more soluble in the solvents, having high dielectric constant.

(c) H_2SO_4 and H_2O_2 have high dielectric constant but these are not a good solvent due to oxidising nature

(II) Ionic reaction –

(a) Ionic compounds shows ionic reaction and covalent compounds shows-molecular reaction.

(b) Ionic reactions are faster than molecular reaction because of free ions.
e.g. When NaCl is added in $AgNO_3$ solution, white ppt of AgCl is formed at once.

$$\underbrace{Ag^+(aq)+N_3^-(aq)}_{AgNO_3\ Sol.} + \underbrace{Na^+(aq)+Cl^-(aq)}_{NaCl Sol.}$$

$$\rightarrow \underset{\text{white ppt}}{AgCl\downarrow} + Na^+(aq) + NO_3(aq)$$

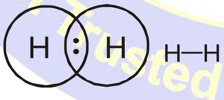
Born-Haber cycle It is an indirect method to calculate the lattice energy of an ionic compound. For example, the lattice energy of sodium chloride can be calculated as follows.

$$\begin{tikzcd}
Na(s) + \arrow[d, "S"] & \frac{1}{2}Cl_2(g) \arrow[r, "\Delta H_{formation}"] \arrow[d, "+D/2"] & NaCl(s) \\
Na(g) + \arrow[d, "IE_1"] & Cl(g) \arrow[d, "-EA_1"] & \\
Na^+(g) + & Cl^-(g) \arrow[uur, "-U"'] &
\end{tikzcd}$$

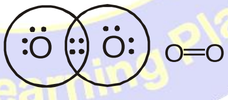
Now, according to Hess's law,
$\Delta H_{formation}$ = S + IE_1 + D/2 – EA_1 – U
Where S is the enthalpy of sublimation of metal (Na), IE_1 is the first ionisation energy of sodium, D is the bond dissociation energy of Cl_2 molecule, EA_1 is the first electron affinity of Cl, U is the lattice energy of NaCl(s) and $\Delta H_{formation}$ is the enthalpy of formation of NaCl.

COVALENT BOND

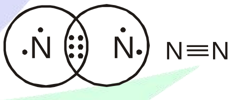
(I) A covalent bond is formed by the mutual sharing of electrons between two atoms of electro negative elements to complete their octet. (Except H which completes its duplet).



H_2 molecule



O_2 molecule



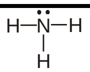
N_2 molecule

(II) The shared pair of electrons which is responsible for the formation of covalent bond is called bond pair of electrons. And valance electrons not involved in sharing are known as non-bonding electrons or lone pair or unshared electrons.

(III) The shared pair of electrons should have opposite spins, and are localised between two atoms concerned.

(IV) Sharing of electrons may occurs in three ways –

No. of electrons shredded between two atoms	Electron pair	Bond
2	1	Single Covalent bond (–)
4	2	Double Covalent bond (=)
6	3	Triple Covalent bond(≡)

Examples –  Three single bonds (not triplet bond)

$H-\ddot{N}(-H)-H$

N≡N Triple bond. (not three bond) O=O Double bond (Not two single bond) H–O–H (Two single bonds.)

Lewis structure and covalent bond :

(I) Electron dot structures, also known as Lewis structures of covalent molecules, are written in accordance with octet rule.

(II) All atoms in a formula will have a total of eight electrons by sharing in the valence shell except the H-atom which forms the largest number of bonds with other atoms placed in the centre of skeleton structure. Other atoms surrounds it to complete the octet.

(III) Structure in which valence electrons are represented by dots are called **Lewis structures**.

(IV) Structure represented by line (–) or dashes are known as coper structure.

(V) Lewis dot formulae show only the number of valency electron, the number and kinds of bonds, but do not depict the three dimensional shapes molecules and polyatomic ions.

Orbital concept of covalent bond :

(I) One orbital can accommodate at the most 2 electrons with opposite spins $\boxed{\upharpoonleft\downharpoonright}$

(II) Half filled orbital or unpaired electron orbital accepts one electron from another atom, to complete its orbitals.

(III) 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.

(IV) **Covalency :** It is defined as the number of electrons contributed by an atom of the element for sharing with other atoms to achieve noble gas configuration.

(V) If the outermost orbit has empty orbitals then covalent bonds are formed in excited state.

General Steps used for writing lewis dot structures :

(I) Calculation of total number of electrons (T) – T is calculated by assuming the octet of each combining atom (duplet in case of H atom).

(II) Calculation of total valence electrons (V) – V is calculated by adding the valence electrons of all the atoms. While doing so, add the unit negative charges (a) for polyatomic anion and subtract the number of unit positive charge (e) in case of polyatomic cation.

(III) Calculation of shared electrons (S) – Total number of shared electrons (S) are calculated from the values of T and V as follows **S = T – V**.

(IV) Calculation of total number of unshared electrons (U) – U is calculated from the values of V and S as follows. U = V – S.

(V) Writing the skeleton structure – This is done by placing the least electronegative atom in the centre and more electronegative atoms on terminal positions. While doing so, some intelligent guess work is also used. H and F atoms are always kept in terminal position.

(VI) Distribution of electrons – Distribute the electrons properly as shared pairs in proportion to total bonds.

Variable valency in covalent bonds :

(I) Variable valencies are shown by those elements which have empty orbitals in outermost shell.

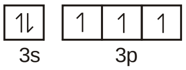
(II) Lone pair electrons gets excited in the subshell of the same to form the maximum number of unpaired electrons. Maximum covalency is shown in excited state.

(III) The energy required for excitation of electrons is called promotion energy.

(IV) Promotion rule – Excitation of electrons in the same orbit.

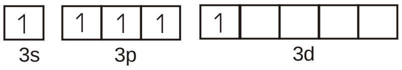
Example –

(a) Phosphorus → Ground state



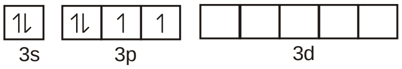
Covalency 3 (PCl_3)

Phosphorus → Excited state



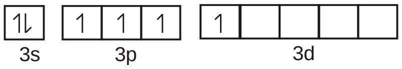
Covalency – 5 (PCl_5)

(b) Sulphur → Ground state.

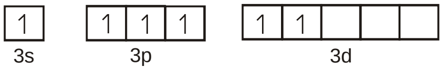


Covalency – 2 (SF_2)

Sulphur → Excited state

1st excited state


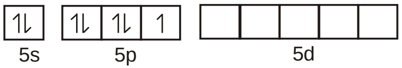
Covalency – 4 (SF_4)

2st excited state


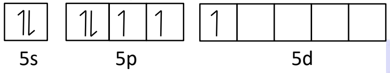
Covalency – 6 (SF_6)

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

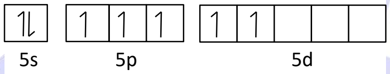
(c) Iodine has three lone pair of electrons

(Ground state)


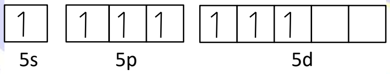
Covalency – 1

1st excited state


Covalency – 3

2nd excited state


Covalency – 5

3rd excited state


Covalency – 7

So it shows three excited states – Maximum number of unpaired electrons = 7
Variable Valencies are 1, 3, 5, 7

SPOT LIGHT

- The maximum covalency is equal to the actual number of s-and p-electrons in the outermost shell.

Applications of Variable Valency :

(I) To explain existence of molecules –

NCl_3 – exists

NCl_5 – doesn't exists (due to absence of d-orbitals in Nitrogen.) While PCl_3 and PCl_5 both exist 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.

(II) Hydrolysis of compounds –

$CCl_4 + H_2O \rightarrow$ No reaction occurs

$SiCl_4 + H_2O \rightarrow$ Reaction occurs

In C-atom there are no empty d-orbitals to accept the lone pair of electrons from water. While $SiCl_4$ has empty 3d-orbitals.

$$SiCl_4 + 4H_2O \xrightarrow[-4HCl]{} \underset{\text{Unstable}}{Si(OH)_4} \longrightarrow SiO_2$$

Example: A covalent bond is possible between -

(1) Similar atom
(2) Dissimilar atoms
(3) Similar and dissimilar atoms
(4) Similar molecules

Solution: **(3)**

It is related to electronegativity.

Example: Why covalent bonds are always directional -

Solution: As the covalent bonds are formed due to overlapping of orbitals which are directional

Example: Which of the following is most covalent -

(1) AlF_3
(2) $AlCl_3$
(3) $AlBr_3$
(4) AlI_3

Solution: **(4)**

As the size of anion increases covalent character increases.

Example: Among LiCl, $BeCl_2$, BCl_3 and CCl_4, the covalent bond character follows the order -

(1) LiCl < $BeCl_2$ > BCl_3 > CCl_4 (2) LiCl > $BeCl_2$ < BCl_3 < CCl_4

(3) LiCl < $BeCl_2$ < BCl_3 < CCl_4 (4) LiCl > $BeCl_2$ > BCl_3 > CCl_4

Solution **(3)**

The covalent character increases according to charge on cation.

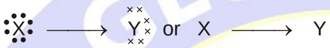
COORDINATE BOND

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

(II) Necessary conditions for the formation of co-ordinate bond are-

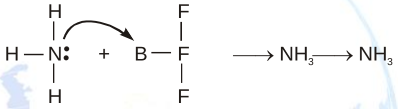
(a) Octet of donor atom should be complete and should have at least one lone pair of electron.

(b) Acceptor atom should have a deficiency of at least one pair of electron.

eg.


(III) Atom which provide electron pair for sharing is called donor.

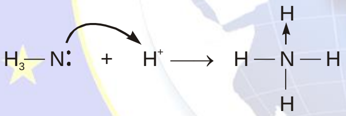
(IV) Other atom which accepts electron pair is called acceptor. That is why it is called donor-acceptor or dative bond



BF_3 is electron deficient compound.

Example:

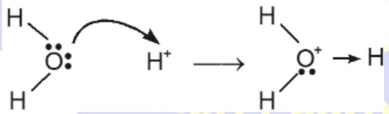
NH_4^+



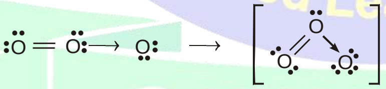
(Lowry - Bronsted acid)

(e^- acceptor)

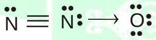
H_3O^+



O_3



N_2O



Compounds in which Ionic, covalent and co-ordinate bonds are present, are as follows-

NH_4Cl, $CuSO_4$, $K_4[Fe(CN)_6]$, KNC, Na_3PO_4, KNO_3, etc

Example: The compound which contains both covalent and co-ordinate bond is -

(1) C_2H_5NC (2) C_2H_5CN (3) HCN (4) None

Solution: **(1)**

Though all compounds have covalent bond but there is coordination bond also between N and C in C_2H_5 NC

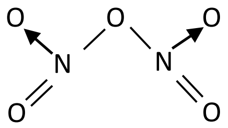
Example: The type of bond present in N_2O_5 are -

(1) Only covalent (2) Only ionic

(3) Ionic and covalent (4) Covalent and coordinate

Solution: **(4)**

The structure of N_2O_5 clears about it

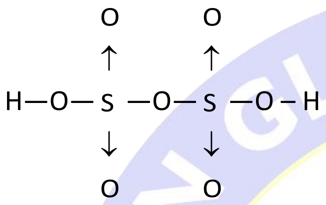


Example: No. of covalent and co-ordinate bond in pyrosulphuric acid are -

(1) 6, 4 (2) 6, 6 (3) 4, 4 (4) 4, 6

Solution: **(1)**

Structure of $H_2S_2O_7$ is as follows



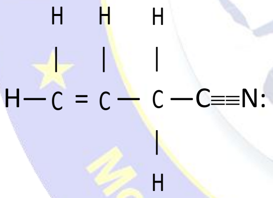
$$\mathrm{H{-}O{-}\underset{\underset{O}{\downarrow}}{\overset{\overset{O}{\uparrow}}{S}}{-}O{-}\underset{\underset{O}{\downarrow}}{\overset{\overset{O}{\uparrow}}{S}}{-}O{-}H}$$

Example: Allyl cyanide has -

(1) 9 sigma bonds and 4 Pi bonds
(2) 9 sigma bonds, 3 pi bonds and 1 lone-pairs
(3) 8 sigma bonds and 5 pi bonds
(4) 8 sigma bonds, 3 pi bonds an 4 non-bonding electrons

Solution: **(2)**

This is clear from structure of allylcyanide



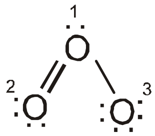
$$\mathrm{H{-}\overset{\overset{H}{|}}{C}{=}\overset{\overset{H}{|}}{C}{-}\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}{-}C{\equiv}N{:}}$$

Formal Charge

The formal charge of an atom in a molecule or ion is defined as the difference between the number of valence electrons of that atom in an isolated or free state and the number of electrons assigned to that atom in the Lewis structure.

$$\boxed{\begin{array}{l}\text{Formal charge (F.C.)}\\ \text{On an atom in a Lewis}\\ \text{structure}\end{array}} = \boxed{\left[\begin{array}{l}\text{Total number of valence}\\ \text{electron in the free atom}\end{array}\right] - \left[\begin{array}{l}\text{Total number of non bonding}\\ \text{(lone pair) electrons}\end{array}\right] - \left(\tfrac{1}{2}\right)\left[\begin{array}{l}\text{Total number of}\\ \text{bonding (shared)}\\ \text{electrons}\end{array}\right]}$$

Let us consider the ozone molecule (O_3). The Lewis structure of O_3, may be drawn as :



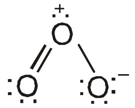
The atoms have been numbered as 1. 2 and 3. The formal charge on :

The central O atom marked 1 = $6 - 2 - \frac{1}{2}(6) = +1$

The terminal O atom marked 2 = $6 - 4 - \frac{1}{2}(4) = 0$

The terminal O atom marked 3 = $6 - 6 - \frac{1}{2}(2) = -1$

Hence, we represent O_3 along with the formal charges as follows :



It should be kept in mind that formal charges do not indicate real charge separation within the molecule. Indicating the charges on the atoms in the Lewis structure only helps in keeping track of the valence electrons in the molecule. **Formal charges help in the selection of the lowest energy structure from a number of possible Lewis structures for a given species.** Generally the lowest energy structure is the one with the smallest formal charges on the atoms.

Note :

(i) The formal charge Is a factor based on a pure covalent view of bonding in which electron pairs are shared equally by neighbouring atoms.

(ii) Pair of +1 and –1 formal charge on adjacent atoms is considered a coordinate bond.

$:\overset{-}{C}\equiv\overset{+}{O}: \Rightarrow :C\overset{\leftarrow}{=}O:$

(iii) Lewis dot structure with minimum formal charges is most stable

FAJAN'S RULE

This rule is used to determine relative ionic & covalent character in a molecule. A molecule is predominantly covalent if

(I) Smaller the size of cation.

(II) larger the size of anion.

(III) greater the charge on cation and anion.

(IV) ion does not have inert gas configuration but it possesses pseudo inert gas configuration (18 electrons in the ultimate shell).

(a) $\xrightarrow[\text{decreasing covalent character due to increase in the size of cation}]{\text{LiCl > NaCl > KCl > RbCl > CsCl}}$

(b) $\xrightarrow[\text{decreasing ionic character because of increase in anionic size}]{\text{NaF > NaCl > NaBr > NaI}}$

(c) $\xrightarrow[\text{increasing covalent nature due to increase of charge on anion and increase in size of anion}]{NaF > Na_2O > Na_3N}$

(d) CuCl and NaCl

$[Cu^+] = [Ar]3d^{10}$; $[Na^+] = [Ne]$

Cations with 18-electron shells (pseudo inert gas configuration) has greater polarising power than 8-electron shell (inert gas configuration) ion with the same charge and size. Thus, CuCl is more covalent than NaCl.

Example: Compound with maximum ionic character is formed from -

(1) Na and Cl (2) Cs and F (3) Cs and I (4) Na and F

Solution: **(2)**

Using fajan's rule, larger cation and smaller anion will have max. Ionic character.

Example: Out of the following which one has the highest values of covalent character -

(1) $ZnCl_2$ (2) $CaCl_2$ (3) $CdCl_2$ (4) CuCl

Solution: **(1)**

Because Zn^{+2} has smallest size among the all.

Example: Compound having highest M.Pt. –

(1) $BeCl_2$ (2) $MgCl_2$ (3) $CaCl_2$ (4) $SrCl_2$

Solution: **(4)**

◆

VALENCE BOND THEORY

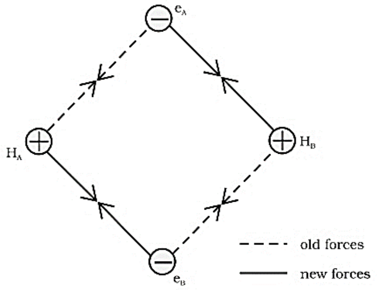
Wave mechanical concept of chemical bonding – (Overlapping)

To explain the nature of covalent bond two theories based on quantum mechanics have been proposed.

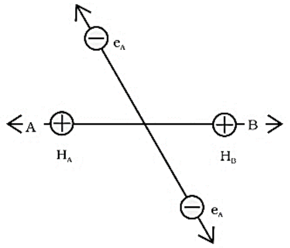
(1) Valence bond theory (VBT) (2) Molecular orbital theory (MOT)

(I) It was presented by Heitler & London (in 1927) to explain how a covalent bond is formed.
It was extended by Pauling & Slater.

Hydrogen molecule



Attractive Forces



Repulsive Forces

(a) Dissociation and formation energy of (H_2) molecules is 435.8 kJ. So that molecule of (H_2) has lower energy than the hydrogen atom (H).
$H_2(g) + 435.8\ kJ \rightarrow H(g) + H(g)$

(b) Now consider two hydrogen atoms A and B approaching each other having nuclei N_A and N_B and electrons present in them are represented by e_A and e_B.

(c) When the two atoms are at large distance from each other, there is no interaction between them. As these two atoms approach each other, new attractive and repulsive forces begin to operate.

(d) Attractive forces arise between:
  (i) Nucleus of one atom and its own electron that is $N_A - e_A$ and $N_B - e_B$.
  (ii) Nucleus of one atom and electron of other atom i.e., $N_A - e_B$, $N_B - e_A$.

Similarly repulsive forces arise between:
  (i) Electrons of two atoms like $e_A - e_B$
  (ii) Nuclei of two atoms $N_A - N_B$.

(e) Attractive forces tend to bring the two atoms close to each other whereas repulsive forces tend to push them apart. Experimentally it has been found that the magnitude of new attractive force is more than the new repulsive forces. As a result, two atoms approach each other and potential energy decreases.

(f) Ultimately force of attraction balances the force of repulsion and system acquires minimum energy. At this stage two hydrogen atoms are said to be bonded together to form a stable molecule.

(g) So the conclusion is energy gets released when the bond is formed between two hydrogen atoms, the hydrogen molecule is more stable than that of isolated hydrogen atoms. The energy so released is called as bond enthalpy.

(II) 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) Resulting bond acquires a pair of electrons with opposite spins to get stability.

(c) Orbitals come closer to each other from the direction in which there is maximum overlapping

(d) So covalent bond has directional character.

(e) In the formation of hydrogen molecule, there is a minimum energy state when two hydrogen atoms are so near that their atomic orbitals undergo partial interpenetration. This partial merging of atomic orbitals is called overlapping of atomic orbitals which results in the pairing of electrons.

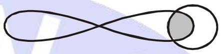
(f) Extent of overlapping $\propto$ strength of chemical bond.

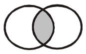
(g) Extent of overlapping depends on two factors.

(I) Nature of orbitals – p, d and f are directional orbitals → more overlapping
s-orbitals → non directional – less overlapping

(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


p - p


p - s


s - s

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

(i) If n is same 2p - 2p > 2s - 2p > 2s - 2s
1s - 2p > 2s - 2p > 3s - 3p

(j) Electron which is already paired in valency shell can enter into bond formation, it they can be unpaired first and shifted to vacant orbitals of slightly higher energy of the same energy shell.

(k) This point can explain the trivalency of boron, tetravalency of carbon, penta valency of phosphorus etc.

(l) Two types of bonds are formed on a count of overlapping.
(A) Sigma (σ) bond (B) Pi (π) bond

(A) Sigma (σ) bond :

(I) Bond formed between two atoms by the overlapping of half filled orbitals along their axis (end to end overlap) is called sigma bond.

(II) σ bond is directional.

(III) σ bond do not take part in resonance.

(IV) Free rotation is possible about a single σ bond.

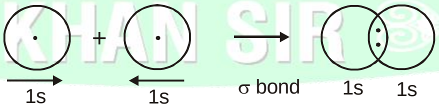
(V) Maximum overlapping is possible between electron clouds and hence it is strong bond.

(VI) There can be only one σ bond between two atoms.

(VII) The order of strength of three types of σ bond [p-p > p-s > s-s].

Sigma bond are formed by four types of overlapping

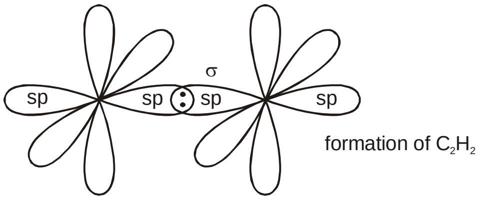
(a) s - s overlapping (H_2) - Two half filled S-orbitals overlap along the internuclear axis.



(Formation of H_2 molecule)

(b) s - p overlapping (Formation of HF) – When half fill s-orbital of one atom overlap with half filled p-orbital of other atom.

(c) Bond between two hybrid orbitals –
$sp^3 - sp^3$, $sp^2 - sp^2$, $sp^3 - sp^2$, $sp^3 - sp$ etc.
overlapping of orbitals form σ bond.



sp-sp hybrid orbital

(d) p - p overlapping – (Coaxial) – It involves the coaxial overlapping between half filled p-orbitals of two different atoms.

eg. Formation of Cl_2, F_2, Br_2

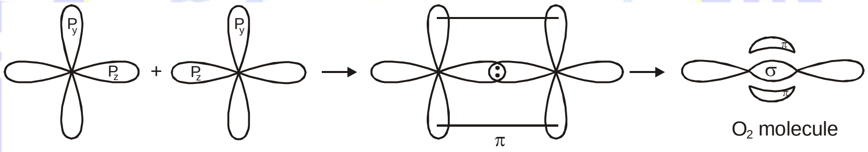
p-p overlapping

(B) Pi (π) bond

(I) The bond formed by sidewise (lateral) overlapping are known as π bonds.

(II) Lateral overlapping is only partial, so bonds formed are weaker and hence more reactive than σ bonds (Repulsion between nucleus is more as orbitals have to come much close to each other for π bonds formation)

Example – Formation of O_2 molecule –



O_2 molecule

Only p_y and p_z of oxygen atom have unpaired e^- in each orbital for bonding.

Electron configuration of oxygen is – $1s^2 2s^2 2p_x^2\ 2p_y^1 2p_z^1$

(III) Free rotation about a π bond is not possible.

(IV) π bond is weaker than σ bond (Bond energy difference is 63.5 KJ or 15 K cal/mole)

(V) π bonds are non-directional, so do not determine the shape of a molecule.

(VI) π bond takes part in resonance.

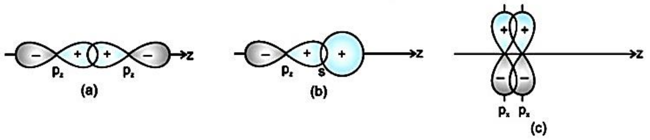
(VII) π bond formed by pure or unhybrid orbitals.

(C) Overlapping of atomic orbitals :

When two atoms approach each other to form a bond, their atomic orbitals overlap. The overlap between the atomic orbitals can be positive, negative or zero depending upon the characteristics of the orbitals participating in overlap.

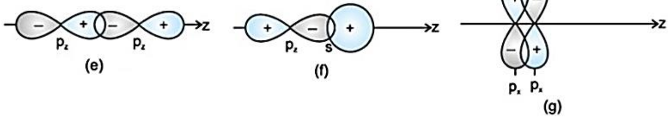
(I) Positive overlap : involves the overlap of the lobes of same signs. It leads to attractive interactions.

Positive Overlap

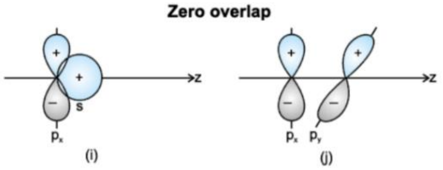


(II) Negative overlap : involves the overlap of the lobes of opposite signs. It leads to repulsive interactions.

Negative or out of phase overlap



(III) Zero overlap : implies inability of any kind of interactions.



Example: Which is not true according to VBT -

(1) A covalent bond is formed by the overlapping of orbitals with unpaired electrons of opposite spins
(2) A covalent bond is formed by the over lapping of orbitals with unpaired electrons of same spin
(3) The greater the extent of overlapping the stronger is the bond
(4) Overlapping takes place only in the direction of maximum electron density of the orbital

Solution: **(2)**

Electrons of same spin never combine to form a bond. Other facts are true for VBT.

HYBRIDISATION

Consider an example of $BeCl_2$ compound :-
If it is formed without hybridisation then -

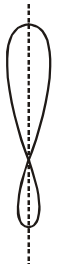
$$\mathrm{Cl}\overset{s-p}{\text{——}}\mathrm{Be}\overset{p-p}{\text{——}}\mathrm{Cl}$$

both the Be–Cl bonds should have different parameters and p-p bond strength >s-p bond strength.
Practically bond strength and distance of both the Be-Cl bonds are same.
This problem may overcome if hybridisation of s and p-orbital occurs.

Hybridisation :

(I) It is introduced by pauling, to explain equivalent nature of covalent bonds in a molecule.

(II) 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.


Structure of hybrid orbital

Now after considering s-p hybridisation in $BeCl_2$

$$\mathrm{Cl}\overset{sp-sp}{\text{———}}\mathrm{Be}\overset{sp-p}{\text{———}}\mathrm{Cl}$$

bond strength of both the bonds will be equal.

Characteristic of Hybridisation :

(I) Hybridisation is a mixing of orbitals and not electrons. Therefore in hybridization full filled, half filled and empty orbitals may take part.

(II) Number of the hybrid orbitals formed is always be equivalent to number of atomic orbital which have taken part in the process of hybridisation.

(III) Each hybrid orbital having two lobes, one is larger and other is smaller. Bond will be formed from large lobe.

(IV) The number of hybrid orbitals on central atom of a molecule or ion = number of σ bonds + lone pair of electron.

- (i) The 1st bond between two atoms will be sigma.
- (ii) The other bond between same two atoms will be pi bond.
- (iii) Maximum two pi bonds may be present on a single atom.
- (iv) The electron pair of an atom which do not take part in bond formation called as lone pair of electron.

(V) One element can represent many hybridisation state depending on experimental conditions for example, C showing sp, sp^2 and sp^3 hybridisation in its compounds.

(VI) Hybrid orbitals are differentiated as **sp, sp^2, sp^3** etc.

(VII) The order of repulsion between Ip & bp is : **Ip - Ip > Ip - bp > bp - bp**

(VIII) The directional properties in hybrid orbital is more than atomic orbitals. Therefore hybrid orbitals form stronger sigma bond. The directional property of different hybrid orbitals will be in following order.
$sp < sp^2 < sp^3 < sp^3d < sp^2d^2 < sp^3d^3$

Difference between hybridisation & overlapping

Overlapping	**Hybridisation**
It occurs between orbitals of two atoms.	It occurs among orbitals of the same atom.
Only half filled orbitals takes part in overlapping.	Any type of orbital can participates.
It occurs during bond formation bond formed after hybridization.	Process, just before overlapping.
Orbital of different energies may participates in excited states. Inground state– NH_3, NCl_3, PH_3, PCl_3	It may takes place in ground or in excited state. Hybridised orbitals are formed

Determination of hybridisation state –

Method (I) : If structure of species is given-

Count the following pair of e^- arround the central atom :

(a) Count all pure σ bonded electron pairs (or σ bonds)

(b) Count all lone pair of electron

(c) Count Co ordinate bond

(d) Count negative charge

Method (II) : If formulae is given-

To predict hybridisation following formula may be used :

No. of hybrid orbital = $\frac{1}{2}$ [Total number of valence e^- in the central atom + total number of monovalent atoms – charge on cation + charge on anion]

eg.

NH_4^+	$\frac{1}{2}[5+4-1]=4$	sp^3 hybridisation
SF_4	$\frac{1}{2}[6+4]=5$	sp^3d Hybridisation
SO_4^{2-}	$\frac{1}{2}[6+2]=4$	sp^3 Hybridization ('O' is divalent so add only charge on anion)
NO_3^-	$\frac{1}{2}[5+1]=3$	sp^2 Hybridization

If such type of e^- pairs are –

Two	sp	hybridisation
Three	sp^2	hybridisation
Four	sp^3	hybridization
Five	sp^3d	hybridization
six	sp^3d^2	hybridisation
seven	sp^3d^3	hybridisation

Types of Hybridisation :

sp hybridisation :

(I) In this hybridisation one s and one p–orbital of an atom are mixed to give two new hybrid orbitals which are equivalent in shape & energy known as sp hybrid orbitals.

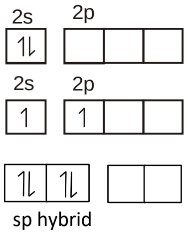
(II) These two sp hybrid orbitals are arrange in straight line & at bond angle 180°.

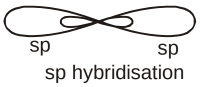
(III) s-character 50%

Be (ground state)

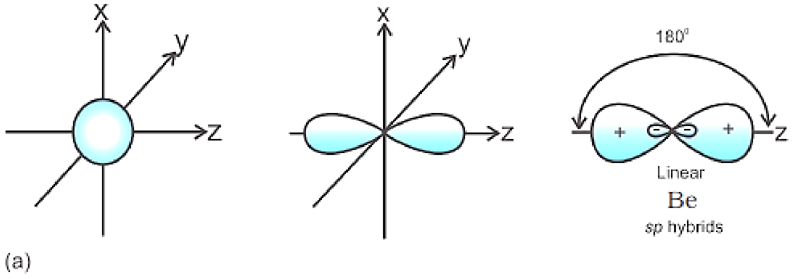
Be (excited state)

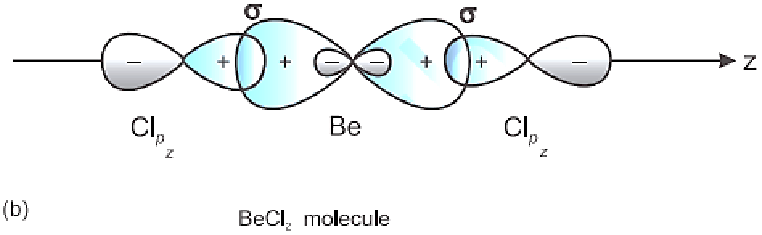
Be atom shares two electrons with two F in $BeCl_2$





sp hybridisation

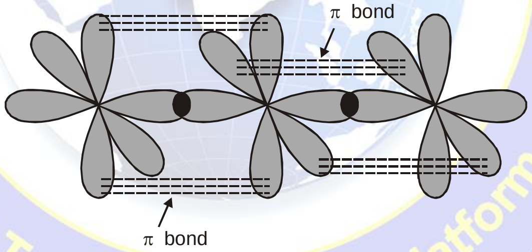




$BeCl_2$ molecule

CO_2 Molecule (O = C = O) :

In CO_2 molecule, C has two sp hybrid orbitals & two unhybridised p orbitals.



Molecular orbital picture of CO_2

Thus, CO_2 molecule is a linear in shape & having 180° bond angle.

The bond length between C–O bond is reduced due to the presence of π bond.

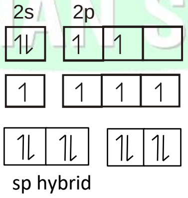
$CH \equiv CH$ $[H–C_A \equiv C_B–H]$

In $CH \equiv CH$ molecules, each C atom contains two sp hybrid orbitals & two unhybridised p orbitals

C(ground state)

C(excited state)

C atom shares four electrons



with H & C, In C_2H_2

sp hybrid orbital of each C overlaps to give sigma bond between C – C.

The remaining one sp hybrid orbital of each C atom overlaps with s orbital of H, forming sigma bond between C – H.

The two unhybridised p orbitals of each C atom (p_y and p_x) overlap laterally to form two pi(π) bonds.

Therefore in $H–C_A \equiv C_B–H$

sigma bond between $C_A – C_B$ is formed sp – sp overlapping

sigma bond between C_A – H is formed sp – s overlapping
sigma bond between C_B – H is formed sp – s overlapping
pi bond between C_A – C_B is formed : $p_y – p_y$, $p_x – p_x$ overlapping
Each C atom forms two sigma bonds but in C_2H_2, total sigma bonds are 3
Each C atom forms two π bonds. Total π bonds in C_2H_2 are two
Total number of bonds in acetylene are :
$3\sigma + 2\pi$ bond = 5 bonds

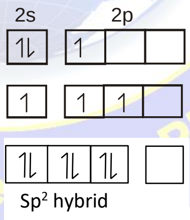
Examples on sp hybridization

Example	σ bond	l.p.e.	Hybridisation	Bond angle	Shape
BeH_2	2	-	sp	180°	Linear
BeF_2	2	-	sp	180°	Linear
$BeCl_2$	2	-	sp	180°	Linear
$BeBr_2$	2	-	sp	180°	Linear
BeI_2	2	-	sp	180°	Linear
CO_2	2	-	sp	180°	Linear
CO	1	1	sp	180°	Linear
C_2H_2	2	-	sp	180°	Linear
HCN	2	-	sp	180°	Linear
$ZnCl_2$	2	-	sp	180°	Linear
$HgCl_2$	2	-	sp	180°	Linear
$CdCl_2$	2	-	sp	180°	Linear
N_2O	2	-	sp	180°	Linear
N_3^-	2	-	sp	180°	Linear

sp^2 Hybridisation :

(I) In this hybridisation one s and two p orbitals are mixed to give three new sp^2 hybrid orbitals which all are in the same shape & equivalent energies.

(II) These three sp^2 hybrid orbitals are at angle of 120° & giving **trigonal planar shape.**



B (ground state)

B (excited state)

B atom shares 3 electrons

with 3 F atoms in BF_3

(III) s - character 33.3%

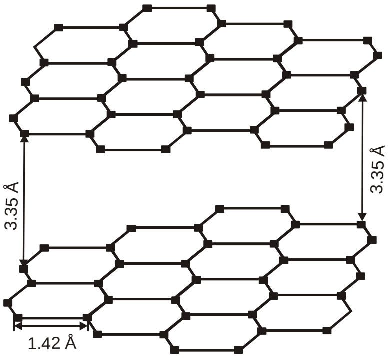
Graphite :

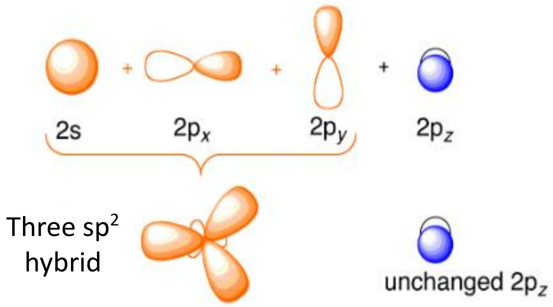
The hybridisation on each carbon atom of graphite is sp^2.

Three sp^2 hybrid orbital are present on each carbon atom at 120° & they overlap to sp^2 hybrid orbitals of adjacent C atoms forming layers of hexagons.

On each carbon atom, one unhybridised. p orbital is also present, which is perpendicular to the plane of sp^2 hybrid orbitals.

The distance between two layer in graphite is 3.35 Å.





Orientation of sp^2 hybrid orbitals.

SnX_2 (X = F, Cl, Br, I)

Sn (ground state) 5s: [⥮] 5p: [↿][↿][ ]

Sn after hybridisation [⥮][⥮][⥮] [ ]
Sp^2 hybrid

shares $2e^-$ with 2 X atoms.

SnX_2 having two σ bonds & one LP electron therefore hybridisation is sp^2
The bond angle is SnX_2 will be less than 120° (due to presence of one LPe.)
The shape of SnX_2 molecule is bent.

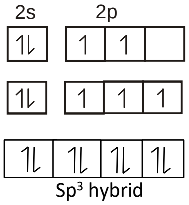
Examples on sp^2 hybridisation

Example	**σ bond**	**l.p.e.**	**Hybridisation**	**Bond angle**	**Shape**
BH_3	3	-	sp^2	120°	Trigonal planar
BF_3	3	-	sp^2	120°	Trigonal planar
BCl_3	3	-	sp^2	120°	Trigonal planar
CH_3	3	-	sp^2	120°	Trigonal planar
$CH_2=CH_2$	3,3	-	sp^2	120°	Trigonal planar
Graphite	3	-	sp^2	120°	Trigonal planar
HNO_3	3	-	sp^2	120°	Trigonal planar
NO_3^-	3	-	sp^2	120°	Trigonal planar
HNO_2	2	-	sp^2	< 120°	Angular (V)
SO_2	2	-	sp^2	< 120°	Angular (V)
SO_3	3	-	sp^2	120°	Trigonal planar
HCO_3^-	3	-	sp^2	120°	Trigonal planar
CO_3^{-2}	3	-	sp^2	120°	Trigonal planar
$SnCl_2$	2	1	sp^2	< 120°	Angular (V)
$SnBr_2$	2	1	sp^2	< 120°	Angular (V)
SnI_2	1	-	sp^2	< 120°	Trigonal planar
$AlCl_3$	3	-	sp^2	120°	Trigonal planar
$GaCl_3$	3	-	sp^2	120°	Trigonal planar
$PbCl_2$	2	1	sp^2	< 120°	Angular (V)

sp^3 Hybridisation :

(I) In this hybridisation one s orbital & three p orbitals of an atom of a molecule or ion, are mixed to give four new hybrid orbitals called as sp^3 hybrid orbitals.

(II) The angle between these four hybrid orbitals will be 109°28’



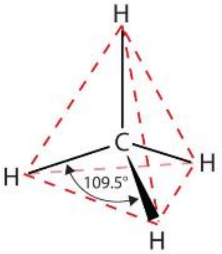
C (ground state)

C (excited state)

C atom shares

four electrons with 4 hydrogen atoms

(III) The shape obtained from these hybrid orbitals would be tetrahedron. Three following examples represent this condition.



(a) Four sigma bonds with zero lone pair electron :

The following examples represent this condition.

CH_4, CF_4, CCl_4, CBr_4, Cl_4, NH_4^+, BF_4^-, AlF_4^-, BeF_4^{-2},

In above compounds, bond angle is 109°28’ & tetrahedron shape.

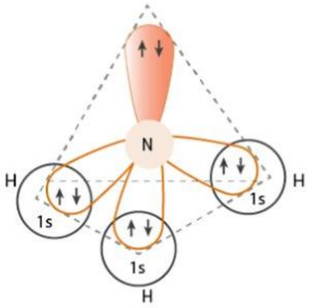
(b) Three sigma bonds & one lone pair of electron :

(I) This condition is shown by following compounds & ions.

NH_3, BiH_3,NF_3,PF_3,NCl_3,PCl_3, CH_3^- ,H_3O^+ ClO_3^-

(II) sp^3 hybridisation, pyramidal shape & bond angle will be less than 109°28' due to the presence of the lone pair electron on nitrogen repels bond pair electron more therefore bond angle is reduced from 109°28’ to 107° in NH_3.

The repulsion between lp – bp > bp – bp.



Orbital overlap in NH_3

(c) Two sigma bonds & two lone pair electrons :

(I) This condition is shown by following compounds and ions.

H_2O, OCl_2, OBr_2, OF_2, OI_2 etc.

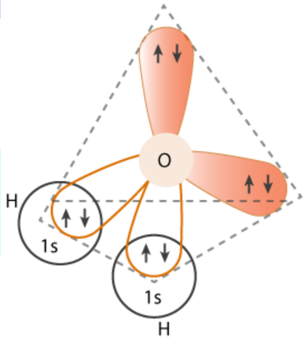
(II) In all above examples, the central atom showing sp^3 hybridisation, angular shape and bond angle will be either less then 109°28’ or more than 109°28’.

In H_2O the hybridisation on O atom is sp^3, but due to presence of two lone pair electrons they repell each other and then repell their adjacent bond pair electron. These repulsion will be in following order.

l.p. – l.p. > l.p. – b.p. > b.p. – b.p.

l.p. = lone pair electron

b.p. = bond pair electron



Orbital overlap in H_2O

Examples on sp^3 Hybridisation

Example	σ bond	l.p.e.	Hybridisation	Shape
CH_4	4	-	sp^3	Tetrahedron
CCl_4	4	-	sp^3	Tetrahedron
CBr_4	4	-	sp^3	Tetrahedron
PCl_4^+	4	-	sp^3	Tetrahedron
NH_4^+	4	-	sp^3	Tetrahedron
BF_4^-	4	-	sp^3	Tetrahedron

AlF_4^-	4	-	sp^3	Tetrahedron
BeF_4^{-2}	4	-	sp^3	Tetrahedron
MgF_4^{-2}	4	-	sp^3	Tetrahedron
$Ni(CO)_4$	4	-	sp^3	Tetrahedron
NF_3	3	-	sp^3	Pyramidal
NCl_3	3	1	sp^3	Pyramidal
$N(CH_3)_3$	3	1	sp^3	Pyramidal
PF_3	3	1	sp^3	Pyramidal
PCl_3	3	1	sp^3	Pyramidal
$AsCl_3$	3	1	sp^3	Pyramidal
$SbCl_3$	3	1	sp^3	Pyramidal
$BiCl_3$	3	1	sp^3	Pyramidal
NH_3	3	1	sp^3	Pyramidal
$:{}^-CH_3$	3	1	sp^3	Pyramidal
H_3O^+	3	1	sp^3	Pyramidal
SO_3^{2-}	3	1	sp^3	Pyramidal
ClO_3	3	1	sp^3	Pyramidal
XeO_3	3	1	sp^3	Pyramidal
H_2O	2	2	sp^3	Angular (V)
H_2S	2	2	sp^3	Angular (V)
NH_2^-	2	2	sp^3	Angular (V)
OF_2	2	2	sp^3	Angular (V)
Cl_2O	2	2	sp^3	Angular (V)
SCl_2	2	2	sp^3	Angular (V)
Diamond	4	-	sp^3	Tetrahedron
SiO_2	4	-	sp^3	Tetrahedron
SiC	4	-	sp^3	Tetrahedron

sp^3d Hybridisation :

(I) In this hybridisation one s orbitals and one d orbital are mixed to give five new hybrid orbitals which are equivalent in shape and energy called as sp^3d hybrid orbitals.

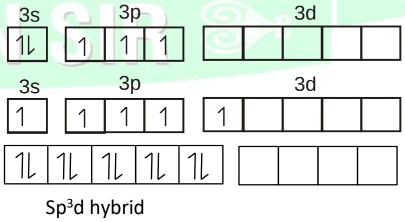
(II) Out of these five orbitals, three hybrid orbitals are at 120° angle and two hybrid orbitals are perpendicular to the plane of three hybrid orbitals that is trigonal planar, the shape of molecule becomes is trigonal bipyrmaidal.

For example, PF_5 showing sp^3d hybridisation

P (ground state)

P* (excited state)

P atom shares five e with Five F atoms



(III) In this hybridisation dz^2 orbital is hybridised with s and p orbitals.

In this way five sp^3d hybrid orbitals form five sigma bond with five F atoms and give a molecule of PF_5, shape of this molecule is trigonal bipyramidal.

Axial two P–Cl bonds are longer than equatorial three P–Cl bond due to repulsion between 3 equatorial bp of e^- and 2 axial b.p. of e^-

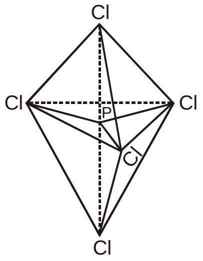
In above hybridisation there are four conditions

(a) Five sigma bonds and zero lone pair electron :

The following examples represent this conditions.

PF_5, PCl_5, PBr_5, PI_5, AsF_5, $AsCl_5$, $SbCl_5$, SbF_5 etc.

The shape of all above molecules is trigonal bipyramidal.



Structure of PCl_5

(b) Four sigma bonds and one lone pair of electron :

The following examples represent this condition.

SF_4, SeF_4, TeF_4, PoF_4, PF_4^-, SbF_4^-, SCl_4, $SeCl_4$, $TeCl_4$ etc.

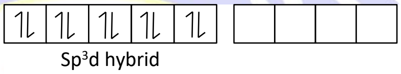
The shape of all above examples will be irregular tetrahedron.

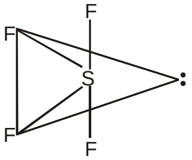
Examples SF_4

S ground state

S excited state

S atom shares four e^- with 4 F atoms





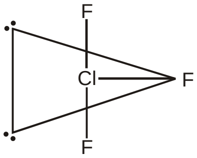
Structure of SF_4

(c) Three sigma bonds & two lone pair of electrons :

The following examples represent this condition.

ClF_3, BrF_3, IF_3, $BrCl_3$, ICl_3 etc.

The shape of all above compounds is 'T' shape.



Structure of ClF_3

(d) Two sigma bonds & three lone pair of electrons :

The following examples represent this condition.

ICl_2^-, IBr_2^-, ClF_2^-, IF_2^-, BrF_2^-, XeF_2^-, I_3^-, Br_3^-

The geometry of above examples will be linear

sp^3d^2 Hybridisation :

(I) In this hybridisation, one s-orbitals, three p-orbitals & two d-orbitals are mixed to give six new hybrid orbitals known as sp^3d^2 hybrid orbitals.

(II) The shape of molecule obtained from above six hybrid orbitals will be symmetrical octahedral.

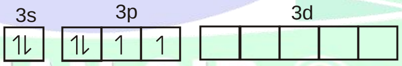
(III) The angle between all hybrid orbitals will be 90°.

Example : SF_6, AlF_6^{-2}, PF_6^-, ICl_5, XeF_4, $XeOF_4$, ICl_4^-,

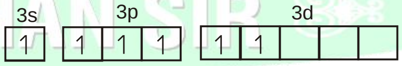
(IV) Two 'd' orbital participates in the hybridisation are d_{x2-y2} and d_{z2}.

SF_6 :

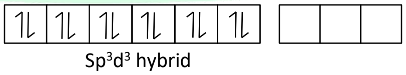
S (ground state)



S (excited state)



S shares six e^-s with 6 F atoms

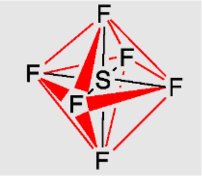


(a) Six sigma bonds and zero lone pair electron :

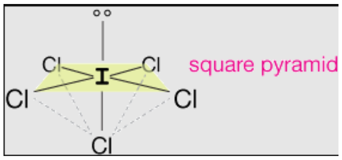
The following examples represent this conditions.

SF_6, AlF_6^{-2}, PF_6^- etc.

The shape of all above molecules is octahedral.



(b) Five sigma bonds and one lone pair electron :

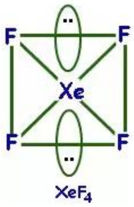


The following examples represent this conditions.

ICl_5, $XeOF_4$ etc.

The shape of all above molecules is square pyramid.

(c) Four sigma bonds and two lone pair electron :



The following examples represent this conditions.

XeF_4, ICl_4^- etc.

The shape of all above molecules is square planar.

sp^3d^3 Hybridisation :

(I) In this hybridisation, one s-orbitals, three p and three d-orbitals are mixed to give seven new hybrid orbitals known as sp^3d^3 hybrid orbitals.

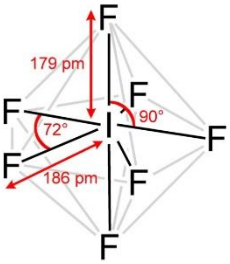
(II) In this hybridisation d-orbitals used are d_{xy} d_{xz} & d_{yz} orbitals.

(III) These seven sp^3d^3 orbitals are configurated in pentagonal bipyramidal shape.

(IV) The following examples showing sp^3d^3 hybridisation –IF_7 & XeF_6.

(V) In IF_7 five electron pair are in same plane at an angle of 72° while other two are perpendicular to the plane, both making an angle of 90° with the plane.

(a) Seven sigma bonds and zero lone pair electron :



The following examples represent this conditions.

IF_7.

The shape of all above molecules is pentagonal bipyramid.

(b) Six sigma bonds and one lone pair electron :

The following examples represent this conditions.

XeF_6.

The shape of all above molecules is disorted octahedral.

Shape of covalent molecules :

- It was given by Sidgwick & Powel.
- According to this concept the shape of covalent compound depends on total pairs of electron (bonded or non bonded) present on the central atom. Which is given as below –

S.No.	Total pair of e^-	Shape	Hybridisation
1.	Two	Linear	sp
2.	Three	Coplaner trigonal (Triangular)	sp^2
3.	Four	Tetrahedral	sp^3
4.	Five	Trigonal bipyramidal	sp^3d
5.	Six	Octahedral (Square bipyramidal)	sp^3d^2
6.	Seven	Pentagonal bipyramidal	sp^3d^3

Example: The hybridization of carbon atoms with C – C single bond of $H-C\equiv C-CH=CH_2$ is -

(1) sp^3-sp^3 (2) sp^2-sp (3) sp-sp^2 (4) sp^3-sp

Solution: **(3)**

As the first carbon has triple bond and second one has double bond with other two carbon atom.

Example: C – C bond in C_2H_6 undergoes heterolytic fission, the hybridisation of carbon is/are -

(1) sp^2 (2) sp^3 (3) sp^2, sp^3 (4) sp, sp^2

Solution: **(3)**

During heterolytic fission there will be formation of CH_3^+ and CH_3^- which has sp^2 and sp^3 hybridization respectively.

Example: The hybridization and geometry of BrF_3 molecule are -

(1) sp^3d and trigonal bipyramidal
(2) sp^3d^2 and Tetragonal
(3) sp^3d and bent
(4) None

Solution: **(1)**

There is one s, three p and one d orbital while hybridization is sp^3d.

VALENCE SHELL ELECTRON PAIR REPULSION (VSEPR) THEORY (GILLESPIE THEORY)

(I) The shape of a molecule is determined by repulsion between the electron pairs (ℓp and bp) present in the valence shell of the central atom.

(II) The order of repulsion is (ℓp-ℓp) > (ℓp-bp) > (bp-bp)

The main postulates of VSEPR theory are as follows:

(I) The shape of a molecule depends upon the number of valence shell electron pairs (bonded or nonbonded) around the central atom.

(II) Pairs of electrons in the valence shell repel one another since their electron clouds are negatively charged.

(III) These pairs of electrons tend to occupy such positions in space that minimize repulsion and thus maximize distance between them.

(IV) The valence shell is taken as a sphere with the electron pairs localising on the spherical surface at maximum distance from one another.

(V) A multiple bond is treated as if it is a single electron pair and the two or three electron pairs of a multiple bond are treated as a single super pair.

(VI) Where two or more resonance structures can represent a molecule, the VSEPR model is applicable to any such structure.

Determination of the Type of Hybridisation :

The number of electron pairs = Bond Pairs + lone pairs (σ Bond)

Table : Shapes of molecules on the basis of VSEPR theory and hybridisation

Total Electron Pairs	Bond Pairs	Lone Pairs	Type of hybridization	Geometry due to repulsion	Bond angle	Example
2	2	0	sp	Linear	180°	$BeCl_2$
3	3	0	sp^2	Trigonal Planar	120°	BF_3
3	2	1	sp^2	Angular	<120°	SO_2
4	4	0	sp^3	Tetrahedral	109°28′	CH_4
4	3	1	sp^3	Pyramidal	<109°28′	NH_3
4	2	2	sp^3	Bent	<109°28′	H_2O
5	5	0	sp^3d	Trigonal bipyramidal	120° & 90°	PCl_5
5	4	1	sp^3d	See Saw	<120° &< 90°	SF_4
5	3	2	sp^3d	Bent T-shaped	< 90°	ClF_3
5	2	3	sp^3d	Linear	180°	I_3^-

6	6	0	sp^3d^2	Octahedral	90°	SF_6
6	5	1	sp^3d^2	Square pyramidal	< 90°	BrF_5
6	4	2	sp^3d^2	Square planar	90°	XeF_4
7	7	0	sp^3d^3	Pentagonal bipyramidal	90° & 72°	IF_7
7	6	1	sp^3d^3	Pentagonal Pyramidal	<90° &<72°	XeF_6
7	5	2	sp^3d^3	Pentagonal Planar	72°	XeF_5^-

Example: In following which central atom has different hybridisation than other –

(1) Cl_2O (2) OF_2 (3) H_2O (4) SO_2

Solution: **(4)**

Because it has sp^2 hybridisation other three have sp^3 hybridisation.

Example: In following hydrocarbon which one has 75% p character and 25% s charater -

(1) C_2H_4 (2) C_2H_2 (3) CH_4 (4) $:CH_2$

Solution: **(3)**

CH_4 because it has sp^3 hybridisation.

Example: Which of the following statement in incorrect -

(1) Non-bonding pairs occupy more space than bonding pairs

(2) The bonding orbitals in a trigonal bipyramidal molecule are described as sp^3d hybrid

(3) $SnCl_2$ has linear shape

(4) PCl_4^+ and $AlCl_4^-$ are isoelectronic

Solution: **(3)**

$SnCl_2$ is a bent shape molecule due to presence of lone-pair of electron other choices are correct.

Example: Shape of NH_3 is very similar to -

(1) CH_4 (2) CH_3^- (3) BH_3 (4) CH_3^+

Solution: **(2)**

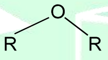
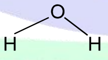
Both have the same state of hybridization with one lone pair of e^- each.

Example: Which of the following has pyramidal shape-

(1) XeO_3 (2) XeF_4 (3) XeF_2 (4) XeF_6

Solution: **(1)**

Due to presence of lone pair of electron.

Example: Ether  and water  have same hybridization at oxygen. What angle would you expect for them -

Solution: In H_2O bond angle is less than 109º28′ due to lone pair and bond pair repulsion. But in ether, due to strong mutual repulsion between two alkyl groups bond angle becomes greater then 109°28′

◆

DIPOLE MOMENT

Dipole moment (μ) = Magnitude of charge (q) × distance of separation (d)

Dipole moment is usually expressed in Debye units (d). The conversion factors are

1 D = 3.33564×10^{-30} Cm, where C is coulomb and m is meter.

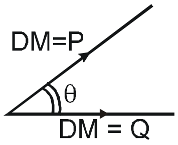
1 Debye = 1×10^{-18} e.s.u. cm.

Further dipole moment is a vector quantity and is depicted by a small arrow with tail on the positive centre and head pointing towards the negative centre. For example the dipole moment of HF may be represented as

$$\overset{+\!\!\!\longrightarrow}{\mathrm{H}-\ddot{\underset{\cdot\cdot}{\mathrm{F}}}:}$$

The shift in electron density is represented by crossed arrow ($\leftarrow\!\!\!+$ ⟶) above the Lewis structure to indicate the direction of the shift.

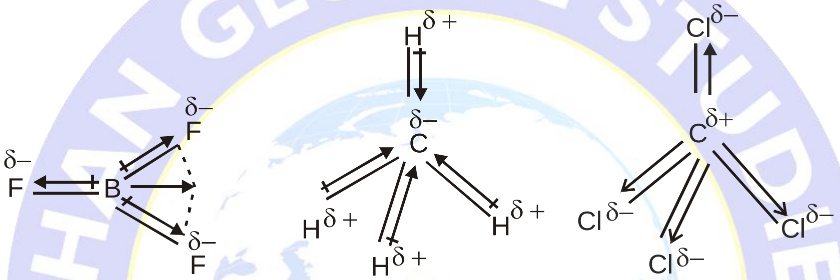
In case of polyatomic molecules the dipole moment not only depend upon the individual dipole moments of bonds known as bond dipoles but also on the spatial arrangement of various bonds in the molecule. In such case, the dipole moment of a molecule is the vector sum of the dipole moments of various bonds. i.e. a molecule will have a dipole moment if the summation of all of the individual moment vector is non-zero.



$R = \sqrt{P^2 + Q^2 + 2PQ\cos\theta}$, where R is resultant dipole moment.

SOME IMPORTANT POINTS ABOUT DIPOLE MOMENT :

1. Again in case of symmetrical molecules such as BF_3, CH_4 and CCl_4 the molecular dipole moment is found to be zero. This is due to the fact that individual dipole moments cancels out on account of symmetry of the molecule.



Following compounds have zero dipole moment :

BF_3, CO_2, SO_3, CF_4, PF_5 (g), SF_6, XeF_2, CS_2, CCl_4, PCl_5 (g), XeF_4

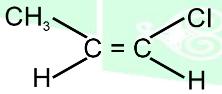
2. A polyatomic molecule having polar covalent bonds but zero dipole moment indicates the symmetrical structure of the molecule. e.g. B - F bonds are polar in BF_3 but BF_3 has $\mu = 0$ due to its symmetrical geometry.

3. If molecule have $\mu = 0$, then it should be linear or having symmetrical geometry.
e.g. linear – CO_2, CS_2, $BeCl_2$ (g) ; symmetrical geometry – BF_3, CH_4, PCl_5, SF_6, IF_7, XeF_4.

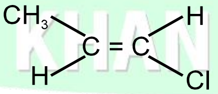
4. If molecule has $\mu \neq 0$ then it should be angular or having unsymmetrical geometry.
$SnCl_2$, $PbCl_2$, SO_2 , angular molecular geometry.
NH_3, H_2O, NF_3, SF_4, H_2S, unsymmetrical molecular geometry.

Note : For geometrical isomers usually the dipole moment of cis is more than trans but again there can be exceptions.

For example :



cis - form (low dipole moment)



trans - form (high dipole moment)

Example: Which of the following bonds is most polar ?

(1) O – H (2) P – H (3) C – F (4) S – Cl

Solution: **(3)**

Due to maximum electronegativity difference.

Example: Bond length of HCl is 1.275 Å (Charge = 4.8×10^{-10} e.s.u.) if $\mu = 1.02$ D, then HCl is -

(1) 100% ionic (2) 83% covalent (3) 50% covalent (4) 40% ionic

Solution: **(2)**

$$\% \text{ ionic character} = \frac{\text{observed } \mu}{\text{theoritical } \mu} \times 100 = \frac{1.02}{1.275 \times 4.8} \times 100 = 17\% \text{ ionic} = 83\% \text{ covalent}$$

Example: The dipole moment of the ammonia molecule is 1.48D. The length of the dipole is -

(1) 3.08×10^{-11} m (2) 5×10^{2} m (3) 308 m (4) None

Solution: **(1)**

$M = 1.48 \times 3.33 \times 10^{-30}$ cm

$= 4.93 \times 10^{-30}$ cm.

$q = 1.6 \times 10^{-19}$C

$$l = \frac{\mu}{q} = \frac{4.93\times10^{-30}}{1.6\times10^{-19}} = 3.08 \times 10^{-11} \text{ m} = 0.0308 \text{ nm}$$

The NH_3 molecule can not have the shape of an equilateral triangle because in the case its dipole moment would equal zero. It is actually constructed in the form of a triangular pyramid with the nitrogen atom at its vertex and the hydrogen atoms at the corners of its base.

MOLECULAR ORBITAL THEORY (MOT):

MOT put forward by Hund & Mulliken, which can be applied to explain the properties, which the old VBT (Valence bond theory) was unable to explain e.g. Paramagnetic nature Of O_2 molecule, as per VBT (**:O: :O:**) it should be diamagnetic.

Definition:

The atomic orbital lose their identity during molecule formation (overlapping) and form new orbitals termed as molecular orbitals.

Characteristic of molecular orbitals:

(I) Molecular orbital formed by overlapping of atomic orbital of same energy

(II) Number of molecular orbital formed = number of atomic orbital involved in overlapping

(III) Half of the molecular orbital have lower energy are called **Bonding** molecular orbital.

(IV) Half are of higher energy - termed as **Antibonding** molecular orbital

(V) Electronic configuration in various molecular orbital are governed by same three rules.

(a) Aufbau's rule (b) Hund's rule (c) Pauli's exclusion principle

Comparison of Bonding molecular orbital & Antibonding molecular orbital :

Bonding molecular orbital (BMO)	Antibonding Molecular orbital (ABMO)
Bonding MO is the result fo the linear combination of AO when their wave function are added $\Psi_b = \Psi_A + \Psi_B$	ABMO is result of linear combination of AO when their wave function are subtracted $\Psi_b = \Psi_A + \Psi_B$
It does not have node.	It always have a node between two nuclei of bonded atom.
Charge density increase between two nuclei resulting attraction between two atoms.	Charge density decrease in between two nuclei, leads to repulsion between two atoms.
Energy of BMO is less, hence stable	Energy of ABMO is high, hence unstable

Notation of molecular orbitals:

As atomic orbitals are known by letters s, p, d and f depending on their shapes. Similarly for molecular orbital.

For bonding molecular orbital- σ, π, δ etc.

For antibonding molecular orbital- $\sigma*, \pi*, \delta*$ etc.

are used for different shapes of electron cloud.

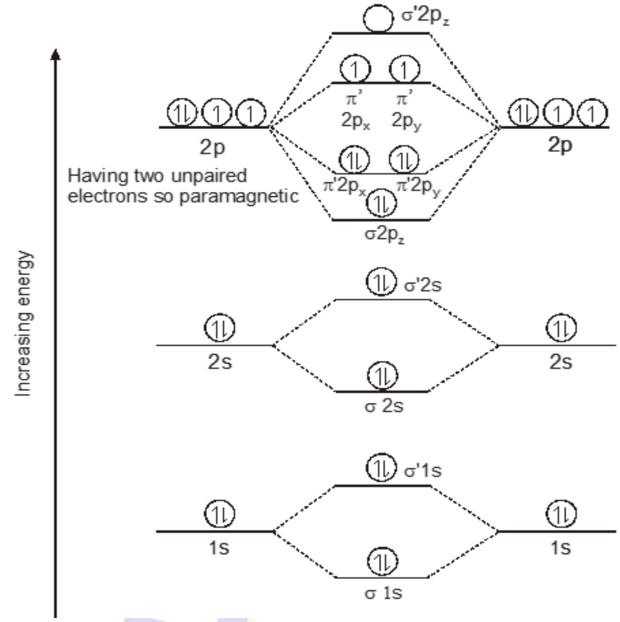
Energy Level Diagram of molecular orbital :

On the basis of Aufbau's rule - increasing order of energies of various molecular orbitals is-

σ 1s < $\sigma*$ 1s < σ 2s < $\sigma*$ 2s < σ 2p$_z$ < π 2p$_x$ ≡ π2p$_y$ < $\pi*$ 2p$_x$ ≡ $\pi*$ 2p$_y$ < $\sigma*$ 2p$_z$

Energy level diagram for homonuclear diatomic molecules like, O_2, F_2, Ne_2

For O_2 molecule-



Having two unpaired electrons so paramagnetic

Bond order = $\frac{1}{2}$ (8 – 4) = 2

Bond order O_2 = 1/2 [8 – 4] = 2
O_2^+ = 1/2 [8 – 3] = 2.5
O_2^- = 1/2 [8 – 5] = 1.5
O_2^{2-} = 1/2 [8 – 6] = 1.5
O_2^{+2} = 1/2[8-2] = 3

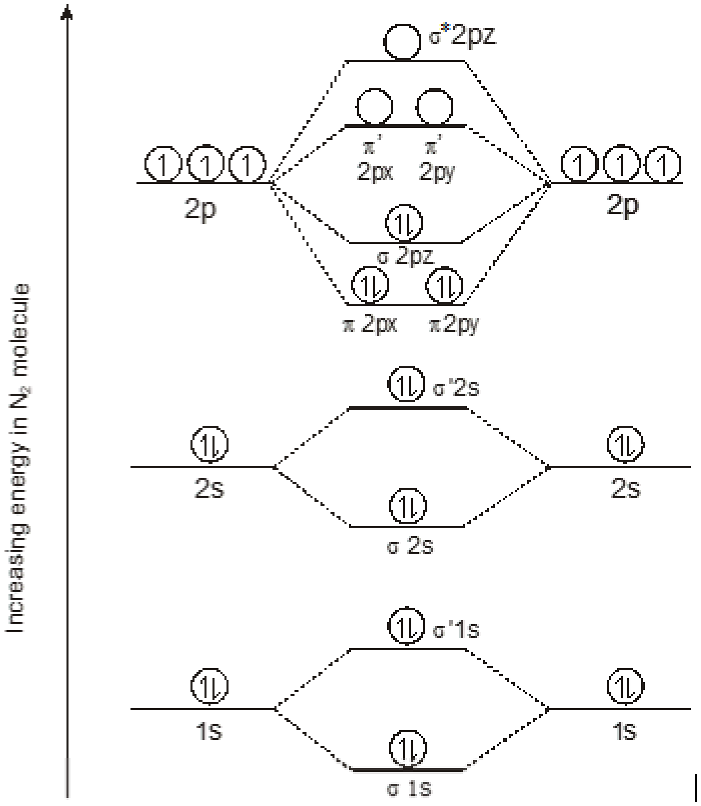
Stability order – $O_2^{+2} > O_2^+ > O_2 > O_2^- > O_2^{2-}$

Bond length – $O_2^{2-} > O_2^- > O_2 > O_2^+ > O_2^{+2}$

Energy level diagram for B_2, C_2 and N_2 molecules –

σ 1s < $\sigma*$ 1s < σ 2s < $\sigma*$ 2s < π2p$_x$ ≡ π2p$_y$ < σ 2p$_z$ < $\pi*$ 2p$_x$ ≡ $\pi*$ 2p$_y$ < $\sigma*$ 2p$_z$

For N_2 molecule



Cause of exceptional behaviour of molecular orbital in B_2, C_2 and N_2:

Energy of 2s and 2p atomic orbitals lie fairly close

Due to small energy difference between 2s and $2p_z$ orbitals, the interaction between them is quite large. This results in loss of energy by σ 2s and $\sigma*$ 2s and thus σ 2s and $\sigma*$ 2s becomes more stable at the cost of σ 2px and $\sigma*$ 2px which gets unestablished (Higher energy).

Electronic configuration of molecules and their related properties :-

for writing electronic configuration of diatomic molecules following two rules to be followed-

Count the number of electrons present in two atoms and then fill in the appropriate energy level diagram according to Aufbau rule.

The pairing in π 2px and π 2py or $\pi*$ 2px and $\pi*$ 2py will take place only when each molecular orbital of identical energy has one electron.

After writing the molecular orbital diagram following parameter about molecules/ion may be predicted.

(i) Bond order :-

Bond order = ½ [No. of electron in bonding molecular orbital ie. N_b
– No. of electron in antibonding molecular orbital ie. N_a] = ½[N_b–N_a]

B.O. = ½ [N_b–N_a]

(ii) Bond length :- (distance between two nuclei)

$$\boxed{\text{Bond length} \propto \frac{1}{\text{Bondorder}}}$$

If $N_b > N_a$ Molecule exists

$$\left.\begin{array}{l} Nb < Na \\ Nb = Na \end{array}\right\} \text{Molecule do not exists}$$

(iii) Stability of molecules - stability $\propto$ Bond order of molecule

(iv) Dissociation energy - Bond dissociation energy $\propto$ Bond order

(v) Magnetic property -

(a) When electron in MO are paired – diamagnetic

(b) When electron in MO are unpaired – paramagnetic

Bonding in molecules :-

(I) Hydrogen molecule-

Having two H atoms with one electron each (1s')

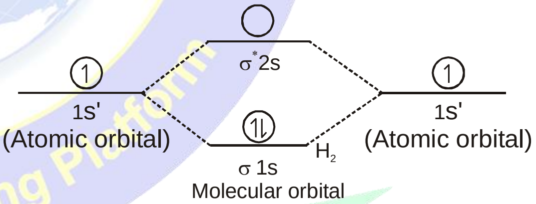
M.O. configuration of H_2 = $(\sigma\ 1s)^2\ (\sigma * 1s)^0$

Bond order = ½ [N_b – N_a]

= ½ [2 – 0] = 1 i.e. single bond

Having paired electron so diamagnetic.

Stability → quite stable (having single bond)



(II) H_2^+ ion –

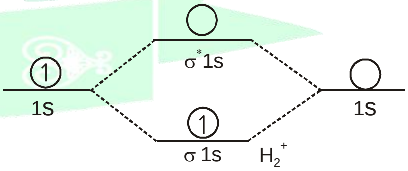
Configuration of $H_2^+ = (\sigma\ 1s)^1\ (\sigma*\ 1s)^0$

One electron in bonding molecular orbital.

So paramagnetic

Bond order = ½ [1– 0] = ½

Less stable



(III) H_2^- anion -

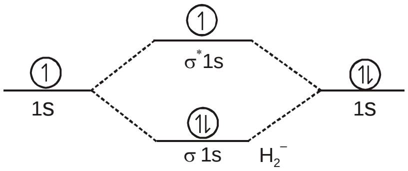
M.O. configuration - $(\sigma\ 1s)^2\ (\sigma*\ 1s)^1$

Paramagnetic

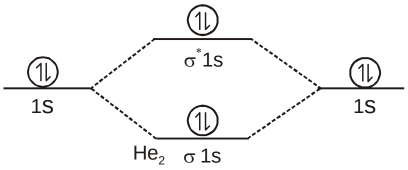
Bond order = ½ [2 – 1] = ½

Stability is less than [H_2^+] because H_2^-

Contain ab ABMO electron



(IV) Helium molecule (He_2) :



M.O. configuration $(\sigma\ 1s)^2\ (\sigma*\ 1s)^2$
Diamagnetic
Bond order = ½ [2 – 2] = 0 (zero)
Bond order zero indicates no linkage between He atoms. Hence He_2 molecule does not exist
Stability (He_2) Highly unstable molecule

Example: The bond order of N_2^- anion is -
(1) 1 (2) 2 (3) 2.5 (4) 3

Solution: **(3)**
Out of 15 e^- in N_2^-, 10 are in bonding MO's and $5e^-$ are in the anti bonding MO's

Hence bond order = $\frac{1}{2}(10 - 5) = 2.5$

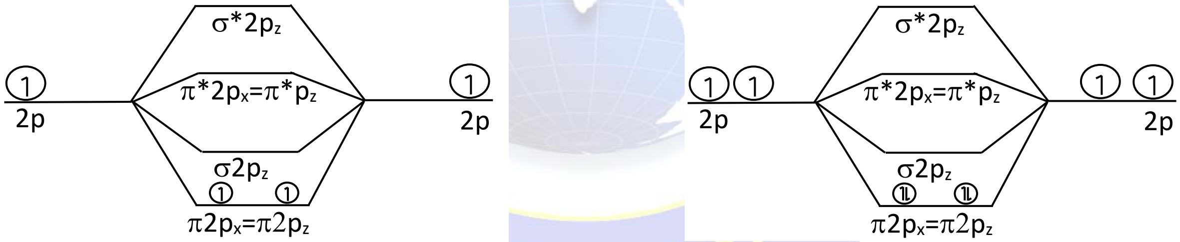
Example: Which of the following has maximum bond strength –
(1) O_2 (2) O_2^+ (3) O_2^- (4) O_2^{2-}

Solution: **(2)**
Bond order of O_2^+ is 2.5 which is maximum among all the species hence its bond strength will also be the maximum.

Example: Which of the molecules B_2 and C_2 has a higher energy of dissociation into atoms? compare the magnetic properties of these molecules.

Solution: We draw energy level diagrams showing the formation of B_2 and C_2 molecules

AO's	MO's	AO's
B	B_2	B
AO's	MO's	AO's
C	C_2	C



Energy level diagrams showing the formation of B_2 and C_2 molecules.

The difference between the number of bonding and the number of antibonding electrons in the B_2 molecule can be seen to be two, and in the C_2 molecule, four. This corresponds to a bond multiplicity of 1 and 2, respectively. Consequently, the C_2 molecule having a higher multiplicity of the bond between the atoms must be more stable. This conchos ion corresponds to the experimentally established values of the energy of dissociation into atoms of the molecules B_2 (276 KJ/mol) and C_2(605 KJ/mol)
In the B_2 molecule, two electrons are arranged, according to Hund's rule, in two $\pi 2p_x$ $\pi 2p_y$ orbitals. The presence of two unpaired electrons imparts paramagnetic properties to this molecule. In the C_2 molecule, all the electrons are paired, consequently, this molecule is diamagnetic

HYDROGEN BONDING

Definition :

(I) It is an electrostatic attractive force between covalently bonded hydrogen atom of one molecule and an electronegative atom (F, O, N)
(II) It is not formed in ionic compounds
(III) H–bond forms in polar covalent compounds, (not in non-polar)

(IV) It is also known as dipole-dipole attraction

$H^{\delta+} — F^{\delta-}$ .... $H^{\delta+} — F^{\delta-}$...... $H^{\delta+} — F^{\delta-}$

Main condition for H-bonding : -

(I) H— should be covalently bonded with high electro–ve element like F, O, N

(II) Atomic size of electro–ve element should be small.

Decreasing order of atomic size is–

$N > O > F$

Decreasing order of atomic electronegativity–

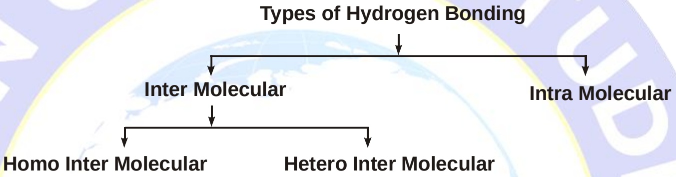
$F > O > N$

(4.0) (3.5) (3.0)

(III) Strength of H–bond $\propto$ Electronegativity of Z (element) $\propto \dfrac{1}{\text{atomic size of Z}}$

(IV) Hydrogen bonding occurs in HCN, due to ($-C\equiv N$) triple bond (sp hybridisation), electronegativities of carbon and nitrogen increases.

$H-C\equiv N$.........$H-C\equiv N$.........$H-C\equiv N$



(1) Intermolecular H–bond

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

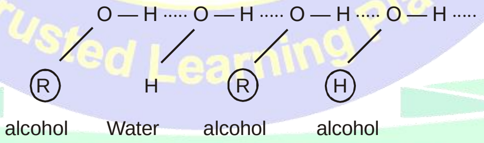
These are two types.

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

eg.

(ii) **Hetero intermolecular :-** H–bond between molecules of different compounds.

eg. alcohol, water



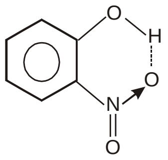
(2) Intra molecular H–bond :- It takes place within the molecule.

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

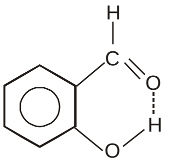
(ii) This type of H–bond is mostly occurred in organic compounds.

(iii) It result in ring formation (Chelation).

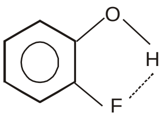
eg.



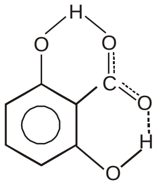
O–nitrophenol



Salicylaldehyde



O–fluorophenol



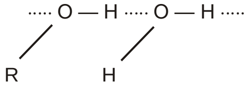
2-6 dihydroxyl benzoate

Effect of H–bond on physical properties :

(I) Solubility

(1) Inter molecular H–bonding

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



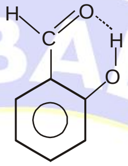
Other examples–Glucose, Fructose etc, dissolve in water.

(b) 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

(c) Solubility order– $CH_3OCH_3 < CH_3OH$

Primary amine > secondary amine > tertiary amine

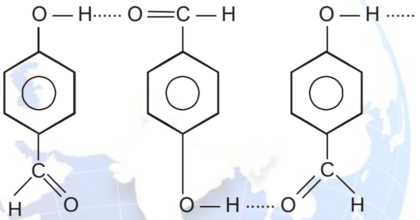
(2) Intra molecular H–bonding:



(a) It decreases solubility as it form chelate by H–bonding, so H–is not free for other molecule.

(b) It can not form H–bond with water molecule so can not dissolves.

(3) Inter molecular H–bond

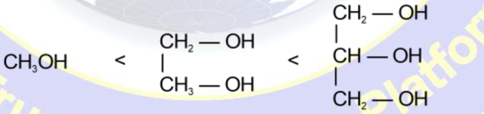


p–hydroxy benzaldehyde

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

(II) Viscosity:

H – bond associates molecules together so viscosity increases



$$CH_3OH < \begin{array}{l}CH_2-OH\\|\\CH_3-OH\end{array} < \begin{array}{l}CH_2-OH\\|\\CH-OH\\|\\CH_2-OH\end{array}$$

H_2O	>	CH_3-OH	>	CH_3-O-CH_3
water		alcohol		ether

(III) Melting point and boiling point

(a) Due to intermolecular H–bond M.P. & B.P. of compounds increases.

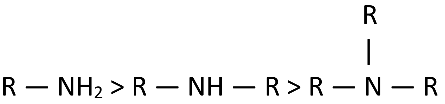
$H_2O > CH_3OH > CH_3-O-CH_3$

(b) Trihydric alcohol > dihydric alcohol > monohydric alcohol

Monocarboxylic acid form stronger H–bond than alcohol of comparable molecular weight. Therefore B.P. of carboxylic acid is higher than alcohol.

(c) Decreasing order of M.P. & B.P. isomer of amines-

1°–amine > 2°–amine > 3°–amine



$R-NH_2 > R-NH-R > R-\overset{\overset{R}{|}}{N}-R$ (no hydrogen with nitrogen atom)

(d) Boiling points of VA, VIA, VIIA hydrides decreases on decreasing molecular weights.

VA VIA VIIA

NH_3	H_2O	HF	b.p.	$HF > HI > HBr > HCl$
PH_3	H_2S	HCl		$H_2O > TeH_2 > SeH_2 > H_2S$
AsH_3	SeH_2	HBr		$NH_3 > SbH_3 > AsH_3 > PH_3$
SbH_3	TeH_2	HI		

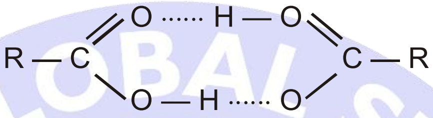
(e) But sudden increase in boiling point of NH_3, H_2O and HF is due to H–bonding

$H_2O > HF > NH_3$ $PH_3 < H_2S < HCl$

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.

(IV) Molecular weight :

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



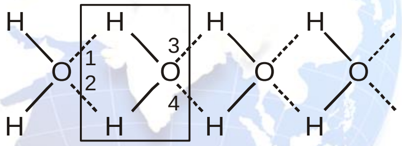
(V) Physical state:

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, from by association of water molecules with the help of H–bond.

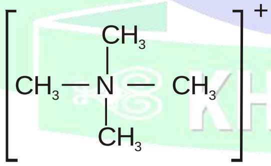
H_2O becomes solid due to four hydrogen bond among water molecule are formed in tetrahedral manner.



(VI) Base strength

CH_3NH_2, $(CH_3)_2$ NH, $(CH_3)_3$ N form H–bond with water. So less hydrolysis i.e. it gives OH^- ions.

While $(CH_3)_4 N^+ OH^-$ (ammonium compound) will give OH^- ion in large amount due to no H–bonding.

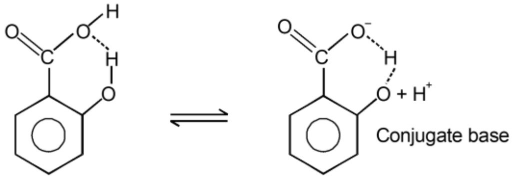


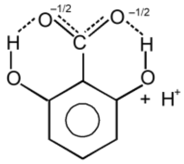
(Ammonium compound.)
NO H–atom bonded directly with N–atom
so no hydrogen bonding occurs.

Effect of intramolecular H–bonding

(I) Strength of acid

(a) The formation of intramolecular H–bonding in the conjugate base of an acid gives extra stability to conjugate base and hence acid strength increases eg. Salicylic acid is stronger than benzoic acid and 2, 6 – dihydroxy benzoic acid > salicylic acid.





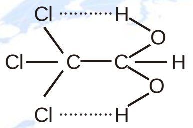
2, 6 dihydroxy benzoate ion

(b) C_2H_5SH is more acidic than C_2H_5OH. In C_2H_5OH, H–bond forms so H^+ is not free

(c) HF is weaker acid than HI, due to H–bond in H – F, H^+ is not free

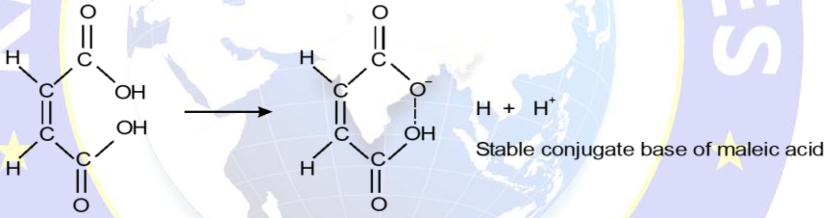
(II) Stability of chloral hydrate:-

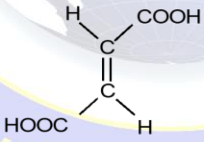
If two or more OH group on the same atom are present it will be unstable, but chloral hydrate is stable (due to H–bonding).



Chloral hydrate

(III) Maleic acid (cis) is stronger acid than fumaric acid (trans).



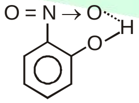


Fumaric acid (No-intramolecular H-bonding)

Example: Which one of the following does not have intermolecular H-bonding -

(1) H_2O (2) o-Nitrophenol (3) HF (4) CH_4

Solution: Nitrophenol has intermolecular H bonding as shown below



Hence (2)

Example: Arrange in increasing order of their boiling point-

HF, HCl, HBr, HI

Which order is correct –

(1)HCl < HBr < HI < HF (2)HCl > HBr > HI > HF (3)HCl < HBr > HI < HF (4) None

Solution: (1)

HCl < HBr < HI < HF

due to strong hydrogen bonding in HF

Vander wall's forces

(a) This type of attractive forces occurs in case of non polar molecules such as H_2, O_2, Cl_2, CH_4, CO_2 etc.

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

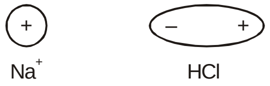
(c) Vander waal force $\propto$ molecular weight

$\propto$ Atomic weight

$\propto$ Boiling point

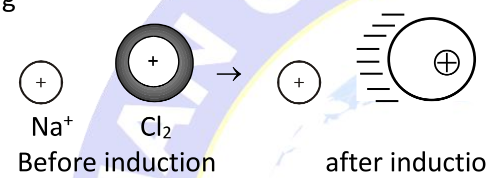
Types of Vander Waal's force : -

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

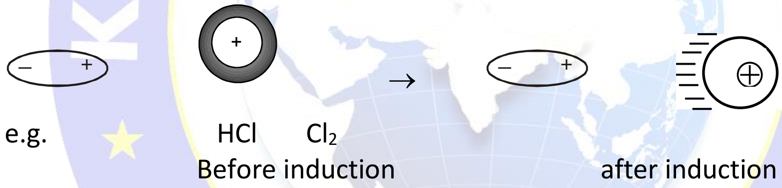


(ii) Dipole Dipole attraction - It is again in between two polar molecules such as HF and HCl

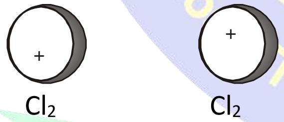
(iii) Ion induced dipole attraction - In this case a neutral molecule is induced by an ion as a dipole as shown in fig



(iv) Dipole - Induced dipole attraction : In this case a neutral molecule is induced as a dipole by another dipole as shown in fig.



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



◆

Bond Parameters

(I) Bond Length (Bond distance) **(II) Bond Angle** **(III) Bond Energy**

(I) 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 A

X_A is electronegativity of A

X_B is electronegativity of B

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

Case II Electronegative difference is not equal to zero then-
Bond length is given by schomaker & Stevenson formula is Bond length = $r_A + r_B - 0.09\,(X_A - X_B)$ Difference in electronegativities

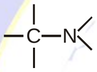
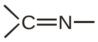
Factors affecting Bond Length :-

(a) **Δ Electronegativity :-** Bond length $\propto \dfrac{1}{\Delta EN}$ (While B.E. $\propto \Delta EN$)

H–F < H–Cl < H–Br < H–I

(b) **Bond order or number of bonds :-** $\boxed{\text{Bond length} \propto \dfrac{1}{\text{Number of bond or bond order}}}$

Bond energy ∝ Number of bond

e.g.	C–C,	C = C,	$C \equiv C$	
Bond length	1.54 Å	1.34 Å	1.20 Å	← increasing
Bond energy	80	140	180–200K.Cal.	increasing →
	C—0	$C{=}O$	$C\overset{\leftarrow}{\equiv}O$	
	1.43 Å	120 Å	1.13Å	
			$C\equiv N$	
	1.47 Å	1.28 Å	1.15 Å	

(c) **Resonance :-** (due to resonance bond length affected)
eg.1. Benzene

C—C bond length 1.54Å
C—C bond length 1.34 Å

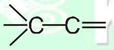
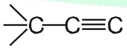
but bond length is between single & double bond is = 1.39 Å

eg. 2 Bond length of C—O in CO_2 is 1.15 Å Resonance occurs in CO_2 a follows-

$$O{=}C{=}O \longleftrightarrow O^{-}{-}C{\equiv}O^{+} \longleftrightarrow O^{+}{\equiv}C{-}O^{-}$$

Bond length = 1.15 Å (Between double & triple bond)

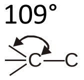
(d) **Hybridisation : -** $\boxed{\textbf{Bond length} \propto \dfrac{1}{\text{s character}}}$

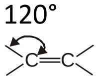
Example : -	Compound	Hybridisation	Bond length
S-character increases ↓	Ethane	sp^3— sp^3	1.54 Å
		sp^3— sp^2	1.51 Å
		sp^3— sp	1.47 Å
	$C{=}C{-}C{=}C$	sp^2— sp^2	1.46 Å
	$C{=}C{-}C{\equiv}C$	sp^2— sp	1.42 Å
	$C{\equiv}C{-}C{\equiv}C$	sp sp	1.37 Å

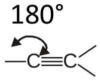
(II) **Bond Angle :-** The angle between any two adjacent bond is known as bond angle. It is represented in degree (°), min (‘) and second (‘’)

Factors affecting the bond angle-

(a) **Number of bond :** Bond angle ∝ Number of bonds (Bond order)







(b) Hybridisation :-

Case 1

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

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

Example :-	CH_4		$\overset{\bullet\bullet}{N}H_3$		$H_2\overset{\bullet\bullet}{\underset{\bullet\bullet}{O}}$
Hybridisation	sp^3		sp^3		sp^3
Bond angle	109	>	107	>	105
	No 1.p.		one 1.p.		two 1.p.

Case-II

When hybridisation is same, bonded atoms are same lone pair is same but central atom is different. Then bond angle ∝ electronegativity of central atom

Example:-	$\overset{\bullet\bullet}{N}H_3$	$\overset{\bullet\bullet}{P}H_3$	$\overset{\bullet\bullet}{As}H_3$
Bond angle	107°	93°	91°

$\xrightarrow{\hspace{4cm}}$

– Electronegativity decreasing

– Bond angle will decrease

Case-III

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

Electronegativity	sp^3	OF_2	103 – 105°
of bonded atom is	sp_3	Cl_2O	109 – 111°
decreasing	sp_3	Br_2O	116 – 118°

Here, $\boxed{\text{bond angle} \propto \frac{1}{\text{electrongativity of bonded atom}} \propto \text{size of side atom}}$

(III) Bond Energy (BE) :- Bond energy may be defined as-

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

(b) **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.

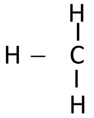
Case-I In diatomic molecule :

Bond energy = bond dissociation energy

eg :- $N_2 > O_2 > H_2 > F_2$

Case-II For polyatomic molecule :-

Bond energy Bond dissociation energy (4)

eg;- 
$H-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-H$ Bond energy = per C—H bond is 99.5 k Cal/mole

Theoretical values of bond dissociation energy (4) of individual C—H bonds CH_4 are given below-

D (CH_3—H)	=	102 k Cal/mole
D (CH_2—H)	=	105 k Cal/mole
D (CH—H)	=	108 k Cal/mole
D (C—H)	=	83 k Cal/mole

Hence bond energy E per C—H bond in methane $= \frac{398}{4}$ = 99.5 K Cal/mole.

Bond dissociation energy (4) is related to the state of hybirdisation.

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 ∝ 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 $\propto \frac{1}{\text{Atomic size}}$

eg. C≡C < C≡N < N≡N

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

Cl — Cl > Br — Br > F — F > I — I

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

Other Example: S – S > O – O or C – C > Si – Si > Ge – Ge

(d) Bond Polarity :- Bond energy ∝ polarity

eg. H—F > H—Cl > H—Br > H—I

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

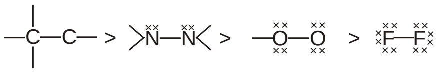
eg. In benzene bond energy of C—C increases due to π electrons of C = C.

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

eg. sp—sp > sp^2—sp^2 > sp^3—sp^3

s. character- 50% 33.3% 25%

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



Size of F and O atoms 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 repels each other in F—F and —O—O— type of bonds.

SPOT LIGHT

- Bond energy of a diatomic molecule is enthalpy change to dissociate one mole of the diatomic gaseous molecule to form the respective gaseous atoms.
- The amount of energy required to break one mole of the bond and separate the bonded atoms in the gaseous state is known as bond dissociation energy.
- The average angle between the bonded orbitals is known as bond angle θ.
- Bond length may be defined as the average distance between the centres of nuclei of two bond atoms.

Resonance

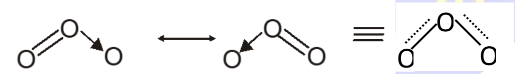
(I) The concept of resonance was introduced by Heisen berg (1920) , and later developed by Pauling and Ingold, to explain the properties of certain molecules,

(II) It has been found that the observed properties of certain compounds cannot be satisfactorily explained by writing a single Lewis structure. The molecule is then supposed to have many structures, each of which can explain most of the properties of the molecule but none can explain all the properties of the molecules. The actual structure is in between of all these contributing structures and is called resonance hybrid and the different individual structures are called resonating structures or canonical forms. This phenomenon is called resonance.

SPOT LIGHT

- The resonance structure do not have independent existence.

(III) Let us discuss resonance in ozone, according to its resonance structure it should have one single bond (O—O = 1.48Å) but experiments show that both the bonds are same which can be proved by its resonance hybrid as shown below.

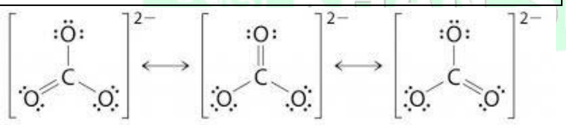


Resonance hybrid

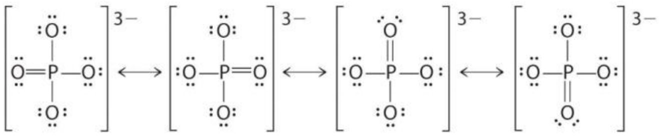
To calculate bond order in the polyatomic molecule or ion use following formula :

$$\boxed{\text{Bond order} = \frac{\text{Total number of bonds in a molecule}}{\text{Resonating Structures}}}$$

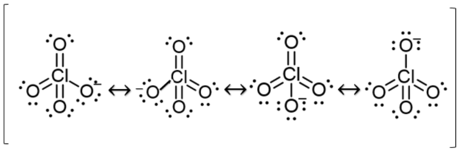
eg.



C—O Bond order $= \frac{4}{3} = 1.33$



P—O Bond order $= \frac{5}{4} = 1.25$



Cl—O Bond order $= \frac{7}{4} = 1.75$

Metallic bond

(a) The constituent particles of metallic solids are metal atoms which are held together by metallic bond.

(b) In order to explain the nature of metallic bond Lorentz proposed a simple theory known as electron gas model or electron sea model.

(c) A metal atom is supposed to consist of two parts, valence electrons and the remaining part (the nucleus and the inner shells) called kernel.

(d) The kernels of metal atoms occupy the lattice sites while the space between the kernel is occupied by valence electrons.

(e) Due to small ionisation energy the valence electrons of metal atoms are not held by the nucleus firmly. Therefore, the electrons leave the field of influence of one kernel and come under the influence of another kernel. Thus the electrons are not localised but are mobile.

(f) The simultaneous attraction between the kernels and the mobile electrons which hold the kernel together is known as metallic bond.

Properties of metals and their explanation by electron sea model :

1. Metallic lusture :

(a) It is due to presence of delocalised mobile electrons

(b) These loosely bonded electrons vibrate due to photon energy of incident light and radiates energy immediately

2. Electrical conductivity :

(a) It is due to mobile electrons.

(b) These electrons flow equally in all direction.

(c) While applying a potential difference across a metal, there will be a directed flow of electrons towards the positive electrode.

(d) The directed flow of electrons carries the electric current from one point to another and therefore, the metals are known to be good conductors.

3. Thermal conductivity :

(a) It can also be explained on the basis of electron gas model.

(b) While heating a metal kinetic energy of electron increases and propagates through collisions.

4. Malleability and ductility :

(a) This property is due to non directional nature of metallic bond.

(b) Basically the kernels can slip over each other when a deforming force is applied.

5. High tensile strength :

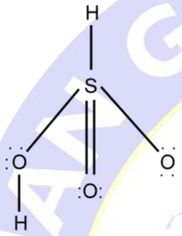
It is due to positively charged kernels and the mobile valence electrons.

DETECTIVE MIND

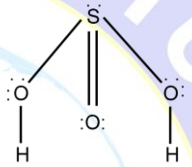
- Strong metallic bonding is favoured by smaller size of kernel.
- Bond theory is related with metallic nature
- The relative strength of various bonds is as follows
  Ionic bond > Covalent bond > Metallic bond > H-bond > Vander waal bond

SPOT LIGHT

- The hydration of ionic compounds involves evolution of heat, weakening of attractive forces and dissociation into ions.
- Many ionic crystals dissolve in water because water decreases the interionic attraction in the crystal lattice due to solvation.
- Hydrogen bond stabilizes the secondary structure of proteins.
- Isoelectronic molecular species have similar molecular orbitals and similar structure according to iso electric principle.
- Polymorphism (Allotropy) is a term used when one and the same substance can crystallise in more than one forms.
- In SO_2 there is $p\pi$ - $p\pi$ bonding as well as $p\pi$ - $d\pi$ bonding due to overlap of filled $p\pi$ orbitals of oxygen with the vacant 3d orbitals of sulphur.
- H_2SO_3 exists in two forms which are always in equilibrium with one another.

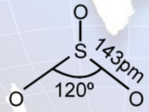


(Unsymmetrical sulphurous acid)

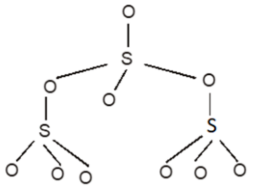


(Symmetrical sulphurous acid)

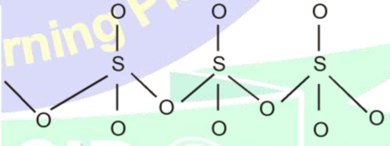
- The unsymmetrical form containing S – H bond explains the reducing character of H_2SO_3.
- The anion of H_2SO_3 i.e. SO_3^{2-} has a pyramidal structure with S atom in sp^3 hybridization and all the S – O bonds are of equal bond length (134 pm)
- In the gas phase, SO_3 is a planar triangular molecule with sulphur atom in sp^2 hybridization state.



- In order to account for the equivalency of all the S – O bonds and short S – O distance of 143 pm, SO_3 may be considered as a resonance hybrid involving $p\pi$-$p\pi$ S – O bonding along with additional $p\pi$-$p\pi$ bonding.
- In the solid phase, SO_3 polymerizes to puckered rings or the more stable layer structure as shown.



Ring structure



Layer Structure

QUICK FOLLOW UP

Chemical Bonding And Molecular Structure

Chemical Bonding, Types of bonds, Theories

Theories of chemical Bonding (Kossel-Lewis approach)

Atoms can combine either by transfer of valence electrons from one atom to another or by sharing of valence electrons in order to have an octet in their valence shell (octet rule)

Types of Bonds

- **Ionic or electrovalent Bond:** Strong electrostatic force of attraction between positive and negative ions.
- **Covalent Bond:** Bond formed by mutual sharing of electrons.
- **Coordinate Bond:** Bond formed when one atom donates a pair of electrons while other simple shares it.
- **Hydrogen Bond:** Attractive force that binds H-atoms directly attached with electronegative atom of other molecule.

Bond Parameters

- **Bond length :** Bond size ∝ Size of atoms, bond length $\propto \frac{1}{bond\ order}$
- **Bond angle:** Angle between the orbitals containing bonding electron pairs around the central around atom in a molecule/complex ion.
- **Bond Enthalpy :** Amount of energy required to break one mole of bonds of a particular type between two atoms in a gaseous state.
- **Bond Order :** Number of bonds formed between two atoms in a covalent compound.

- **% ionic character :** Percent ionic character $\propto \frac{Actual\ dipole\ moment\ of\ the\ bond}{dipole\ moment\ of\ a\ pure\ ionic\ bond} \times 100$
- Percent ionic character can also be calculated by using, Pauling equation = $18(X_A - X_B)^{1.4}$
  Hannay and Smith equation : = $16(X_A - X_B) + 3.5(X_A - X_B)^2$

Theories of Covalent Bonding

VSEPR Theory

- Nyholm and Gillespie
- The shape of a molecule depends upon the number of valence shell electron pairs (bonded or non-bonded) surrounding the central atom.
- Electron pairs tend to occupy such positions in space which minimize repulsions.
- The repulsive interactions of electron pairs decrease in the order: lp – lp > lp – bp > bp – bp

Molecular Orbital Theory

- F. Hund and R.S. Mulliken
- Molecular orbitals are formed by the linear combination of atomic orbitals.
- When two atomic orbitals combine they form one bonding molecular orbital of lower energy and one anti-bonding molecular orbital of higher energy.
- The molecular orbitals are filled in accordance with Aufbau principle.
- Stability of molecule : If $N_b > N_a$, molecule is stable and if $N_b > N_a$, molecule is unstable.

Valence Bond Theory (Pauling)

A covalent bond is formed by overlapping of singly occupied atomic orbitals of valence shell of two atoms.

Hybridisation

sp hybridisation
Shape : Linear
Examples : $BeCl_2$, C_2H_2
Bond angle : 180°

sp^2 hybridisation
Shape : Trigonal planar
Examples : BCl_3, C_2H_4
Bond angle : 120°

sp^3 hybridisation
Shape : Tetrahedral
Examples :
CH_4 (Bond angle : 109°28’)
NH_3 (Bond angle : 107°)
H_2O (Bond angle : 104.5°)

sp^3d hybridisation
Shape : Trigonal bipyramidal
Examples : PF_5, PCl_5
Bond angle : 120° and 90°

sp^3d^2 hybridisation
Shape : Octahedral
Examples : SF_6, UF_6, TeF_6
Bond angle : 90°

sp^3d^3 hybridisation
Shape : Pentagonal bipyramidal
Examples : IF_7, XeF_6
Bond angle : 72° and 90°