3. CHEMICAL BONDING AND MOLECULAR STRUCTURE

SYNOPSIS:

The force of attraction between atoms or ions is called chemical bond.

- Chemical bonds are of many types
  a) Ionic bond b) Covalent bond
  c) Co-ordinate covalent bond d) Metallic bond, etc.
- Formation of chemical bonds involved electrons and nuclei and mainly energy changes.
- Bond formation is exothermic and bond breaking is endothermic.
  $H + H \rightarrow H - H + 104$ k.cal ; $H - H \rightarrow H + H - 104$ k.cal
- Bonds are formed between atoms or ions to gain stability.
- In the bond formation, some energy is released and potential energy of system decreases.
- The two bonded atoms are at optimum or equilibrium distance. So that the attractive and repulsive forces are balanced.
- If the bonded atoms approach much closer beyond the equilibrium distance, the repulsive forces will exceed the attractive forces.
- In exothermic reaction, the number of bonds formed in the products is greater than number of bonds broken in the reactants (or)
- Strong bonds are formed in the products and weak bonds are broken in the reactants.
- Molecules are more stable than individual atoms.

Electronic Theory of Valency:-

- This was proposed by Kossel and Lewis.
- This theory explains how and why the bonds are formed.
- Valence electrons are responsible for bonding process.
- Inert gases have $ns^2\ np^6$ configuration but, Helium has $1s^2$. Thus, all inert gases have octet and helium has duplet configuration.
- Noble gases are chemically inert and will not take part in bonding because they are stable due to octet configuration in the valence shell.
- Atoms of all other elements contain less than 8 electrons in valence shell.
  $\therefore$ These elements are chemically reactive and take part in chemical reactions to become stable by attaining octet configuration.
- Attaining octet configuration in the valence shell is called octet rule or octet theory.
- Some elements may become stable by attaining duplet configuration e.g. H, Li, Be.
- Octet configuration can be achieved by loosing or gaining or mutual sharing of electrons.
  As per this theory, core electrons will not take part in bonding.
  Atom - Valence = Core

VALENCE or VALENCY:

It is the combining capacity of an element i.e., number of bonds formed by the element.

Valence of an element = group number or

(8 - group number)

IONIC BOND

(Electrostatic bond or electrovalent bond):

- Ionic bond was explained by Kossel.
- The strong electrostatic force of attraction between oppositely charged ions which are formed by the transfer of the electrons is called Ionic bond.
- Ionic bond is formed between different atoms
  i.e atoms of different electronegativities.

It is generally formed between metal atom and non-metal atom.

- It cannot be formed between same or similar atoms.
- There is no 100% ionic compound. Most ionic compound is CsF (Cesium fluoride)
- To form an ionic bond, the electronegatives between combining atoms should be greater than 1.7.
- Ionic bond is generally formed between electropositive and electronegative element or less electronegative and more electronegative elements.
  Ionic bond is generally formed between
  IA and VIIA group
  IA and VIA group
  IIA and VIIA group
  IIA and VIA group

Ionic bond is non-directional as it involves electrostatic attraction.

FACTORS FAVOURABLE FOR IONIC BOND FORMATION

- The ease of formation of ionic bond depends on the case of formation of cation and anion.

Conditions favourable for cation	***Conditions favourable for anion***
1) **Size:** Larger atoms will form cations readily Eg.: Li < Na < K < Rb < Cs	**Size:** Smaller atoms will form anion readily Eg.: F > Cl > Br > I
2) Ionisation potential: Atoms with low I.Ps will form cations readily. Eg.: Na > Mg > Al IP $\rightarrow$ increases Ease of formation decreases.	**Electron affinity:** Atoms with high electron affinity will form anion readily. Eg.: Cl > Br > I Electron affinity decreases Ease of formation decreases.
3) **Charge:** Cation with less positive charge is readily formed Eg.: $Na^{+} > Mg^{2+} > Al^{3+}$ Ease of formation increases with decrease in the charge.	**Charge:** Anion with less negative charge is readily formed. Eg.: $F^{-} > O^{-2} > N^{-3}$ Ease of formation increases with decrease in the charge.
4) **Electronic configuration:** Cation with inert gas configuration is more stable and more readily formed than cation with pseudo inert gas configuration	

a) Ca^{+2} > Zn^{2+}
2, 8, 8 2, 8, 18
Inert gas configuration Pseudolnert gas configuration

b) Na^+ > Cu^+
2.8 2.8.18
Inert gas configuration Pseudolnert gas configuration
Higher lattice energy also favours ionic bond formation

LATTICE ENERGY:- (ν)

The amount of energy released when the oppositely charged gaseous ions combine to form one mole of solid ionic crystal (or)

The amount of energy absorbed to separate one mole of solid ionic crystal into oppositely charged gaseous ions is called lattice energy.

$Na^+_{(g)} + Cl^-_{(g)} \rightarrow NaCl_{(s)} + 184.2$ kcal

$\rightarrow NaCl_{(s)} + 782$ KJ/mole

$NaCl_{(s)} \rightarrow Na^+_{(g)} + Cl^-_{(g)} - 782$ KJ/mole

- In a given ionic crystal, there are attractions between opposite charges and repulsions between electron clouds of cation and anion.
- Thus, lattice energy is the sum of potential energy due to attractions and potential energy due to repulsions.

$$PE_{att}n = -\frac{NAZ^+Z^-e^2}{r}$$

$$PE_{rep}n = +\frac{NBe^2}{r^n}$$

Lattice energy (u) $= -\frac{NAZ^+Z^-e^2}{r} + \frac{NBe^2}{r^n}$

Where N → Avagadro's number
A → Madelung's constant
Z^+ → Positive charge
Z^- → Negative charge
e → Charge of e^-
B → Repulsive co-efficient
n → Born exponent

- Lattice energy is inversely proportional to the sum of radii of cation and anion.

$$u \propto \frac{1}{r^+ + r^-}$$

u ∝ charge,

$$u \propto \frac{1}{size}$$

- Generally, the ion, (cation or anion) with **smaller size and more charge will have greater lattice energy.**

Born-Haber's cycle:

The basis for Born-Haber's cycle is Hess's law. It states that the heat energy change will remain constant whether a chemical reaction occurs in one step or several steps.

Lattice energy cannot be determined by direct experimental methods.

- But it can be determined by using Born- Haber's cycle. Eg.: Formation of NaCl

1st way:

$$Na(s) + \frac{1}{2}Cl_2(g) \rightarrow NaCl(s)$$

(Q = - 410.5 KJ / mole)

- One mole sodium reacts with half mole chlorine gas to form solid NaCl crystal.

2nd way:

1) Sublimation of sodium.
   Solid sodium on heating directly changes to vapour state and the heat energy is called sublimation energy.
   $Na_{(s)} \rightarrow Na_{(g)} + S$ (ΔH = 108.7 KJ/mole)

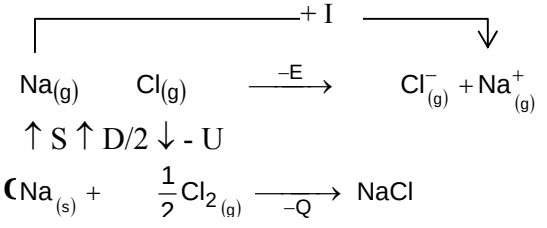
2) Dissociation of Cl_2
   Cl_2 molecule dissociate into Cl - atoms.
   The energy required for dissociation of molecules into atoms is called dissociation energy.
   $\frac{1}{2}Cl_{2(g)} \rightarrow Cl_{(g)} + \frac{D}{2}.\ (\Delta H = 119.55 KJ/mol)$

3) Ionisation of Na
   Electron is removed from Na to form sodium cation.
   $Na_{(g)} \xrightarrow{-e^-} Na^+_{(g)} + IP.\ (\Delta H = 492.8 KJ/mol)$

4) Electron affinity of Cl :
   Neutral gaseous Cl atom gains an e^- to give Cl^- ion and the energy released is called EA.
   $Cl_{(g)} \xrightarrow{e^-} Cl^-(g) - EA\ (\Delta H = -361.57 KJ/mol)$

5) Lattice energy :
   $Na^+_{(g)}$ and $Cl^-_{(g)}$ will combine to form one mole of solid ionic crystal of NaCl. Energy released in the process is called lattice energy.
   $Na^+_{(g)} + Cl^-_{(g)} \rightarrow NaCl_{(s)} \pm U$
   Acc. to Hess' law,
   $-Q = +S + \frac{D}{2} + I - E - U$
   $-410.5 = 108.7 + 119.5 + 492.82 - 316.57 - U$
   $\therefore U = -770$ KJ / mole

   All the above changes can be schematically represented in the form of following cycle.



The three dimensional network in which the cations and anions are arranged at optimum distances is called crystal lattice.

Co-ordination number :

The number of oppositely charged ions that surround a particular ion in the ionic crystal.

Generally, a cation is surrounded by specific number of anions and anion is surrounded by a specific number of cations.

a) Co-ordination number of NaCl is 6.
Each Na^+ ions is surrounded by $6Cl^-$ ions and each Cl^- ion by 6 Na^+ ions.

b) Co-ordination number of CsCl is 8.

- In some ionic crystals like CaF_2 and Na_2O, co-ordination numbers are different for cation and anion.
  Eg: 1) CaF_2
  co-ordination number of Ca^{2+} is 8.
  F^- is 4.
  2) Na_2O
  co-ordination number of Na^+ is 4.
  O^{2-} is 8.
- The co-ordination number of any ionic crystal depends on ratio of size of cation to size of anion.
  $\frac{r_c}{r_a}$ = limiting radius.
  With increase in $\frac{r_c}{r_a}$, i.e. with increase in size of cation, co-ordination number increases.

$\frac{r_c}{r_a}$	co-ordination number	**Examples**	**Shape**
upto 0.155	2	–	Linear
0.155 - 0.225	3	B_2O_3	Trigonal Planar
0.225 - 0.414	4	ZnS	Tetrahedral
0.414 – 0.732	6	NaCl	Octahedral (F.C.C)
0.732 - 0.999	8	CsF, CsCl	B.C.C.

Most common co-ordination numbers are 6 and 8.

UNIT CELL:

Smallest fraction of crystal lattice which gives the whole lattice arrangement is called unit cell.

These unit cells in repetitions in 3 dimensions will give entire crystal lattice

CRYSTAL STRUCTURE OF NaCl: NaCl has face centered cubic lattice structure (FCC)

- Co-ordination number is 6 because $\frac{r_c}{r_a}$ is 0.52. Each Na^+ ion is surrounded by six Cl^- and each Cl^- ion is surrounded by 6 Na^+ ions.
- The number of formula units or molecules or ion pairs of NaCl for unit cell = 4.
  Contribution of body central Na^+ ion towards 1 unit cell = $1 \times 1 = 1$.

Contribution of Na^+ ion on edges towards 1 unit cell = $12 \times \frac{1}{4} = 3$.

Contribution of face central ions towards 1 unit cell = $6 \times \frac{1}{2} = 3$.

Contribution of corner ions towards one unit cell = $8 \times \frac{1}{8} = 1$.

CRYSTAL STRUCTURE OF CsCl : CsCl has body centered cubic lattice [BCC]

Its co-ordination number is 8 $\because \frac{r_c}{r_a} = 0.92$

Each Cs^+ ion is surrounded by 8 Cl^- ions and vice versa.

Number of ion pairs or formula units or molecules per unit cell = 1.

Contribution of body centred Cs^+ ion towards one unit cell = 1 × 1 = 1

Contribution of corner Cl^- ions towards one unit cell = $8 \times \frac{1}{8} = \frac{8}{8} = 1$

Properties of Ionic compounds:

1) Physical state :
   They exist as crystalline solids due to close packing structure and strong interionic attractions.
2) Melting and boiling points:
   Ionic compounds have high MPs and BPs due to strong interionic attractions.
3) Electrical conductance:
   Ionic compounds are good conductors in fused or aqueous state due to presence of ions and free flow of ions.
4) Ionic bond is non-directional in nature :
   As the ionic bond is non directional in nature. Ionic compounds do not exhibit space isomerism.
5) Reactions of Ionic compounds :
   Reactions in between Ionic compounds are very fast in aqueous solution because they does not involve any reshuffling of bonds. In aqueous solution, ions are free and they are just exchanged in reaction.
6) Solubility:
   Ionic compounds dissolve in polar solvents like H_2O due to ion-dipole interactions. Ionic compounds are generally insoluble in non-polar solvents like $CHCl_3$, CCl_4, CH_3OH, C_6H_6, etc.

Covalent bond:

It was proposed by Lewis. The bond formed by sharing of electron pair is called covalent bond.

In covalent bonding, both atoms will contribute and both will share.

Covalent bond can be formed between same atoms or different atoms.

- Maximum number of bonds (covalent) formed between 2 atoms is 3. But, an atom can form bonds upto 8.
- Pure or 100% covalent bond is the bond formed between same atoms.
- With decrease in electronegativity, difference, the tendency to form covalent bonds increase.

Favourable conditions for formation of covalent bond: [Fazan's rule]

- Cation should be smaller and anion should be larger in size.
- Cation with more positive charge and anion with more negative charge will favour covalent bonding.
- The electronegativity difference should be less than 1.7 in between combining atoms to form covalent bonds

The purpose of forming covalent bonds in between the atom is to attain stability by attaining noble gas configuration.

Covalent bond is denoted by "—"

Eg.: Homonuclear diatomic molecule.

Covalency:

It is the number of electrons contributed by an atom or the number of covalent bonds formed by an atom

Covalency:

H_2	covalency of hydrogen is	1
O_2	covalency of oxygen is	2
N_2	covalency of nitrogen is	3
H_2O	covalency of oxygen is	2
H_2O	covalency of hydrogen is	1
NH_3	covalency of nitrogen is	3
CO_2	covalency of carbon is	4
PCl_5	covalency of phosphorous is	5
SF_6	covalency of sulphur is	6

Properties of covalent compounds:

- They exist as either gases or liquids due to weak Vanderwaal's forces.
- MP_s and BP_s are very low due to weak Vanderwaals forces in between the molecules.
- Electrical conductance :
- They are bad conductors as they donot contain ions.
- Due to directional nature of covalent bond, covalent compounds exhibit Isomerism
- The reactions in between covalent compounds are slow because they involve breaking and making of bonds.

Solubility:

They are soluble in non-polar solvents like CCl_4, chloroform, C_6H_6 and insoluble in polar solvents like water.

Exceptions to the above properties:

Certain covalent compounds like sugar, urea, glucose, etc will exist as crystalline solids due to strong inter-molecular forces i.e. may be H bonds.

- Some covalent compounds like HCl, HF, HI, etc. are good conductors because they are polar and ionise in water.
- Some covalent compounds like sugar, urea, glucose, alcohol, HF are soluble in polar solvents like water due to H̃ bonding.

Best solvent for Ionic and covalent substances is liquid ammonia.

Best solvent for Ionic and polor solvents is water.

Exceptions to Octet rule (or) Failures of Lewis theory:-

- There are many molecules which donot obey the octet rule i.e., having less than 8 or more than 8 e^- s in the valence shell of central atom.

  Ex: $BeCl_2$ (4 e^- s); BCl_3 (6 e^- s); PCl_5 (10 e^- s) SF_6 (12 e^- s)
- It fails to explain single electron or odd electron bond.
- Eg : H_2^+ single e^- bond. Odd e^- bond: O_2^-, NO, NO_2, ClO_2
- It could not explain the shapes and bond angles of various molecules.
- Transition elements generally disobey the octet rule.

Valence bond theory:

The basis of VBT is Schrodinger's wave equation i.e. wave mechanics. It explains shapes of covalent molecules and strength of covalent bonds.

- This theory was proposed by Hietler and London and developed by pauling and slater.

Postulates: A bond is formed by the overlapping of two half-filled orbitals of two atoms.

- The e^-s in the overlapping orbitals must be with opposite spins.
- Strength of covalent bond will depend on the extent of overlapping i.e., greater the extent of overlapping, stronger is the bond formed and vice versa.
- The direction in which overlapping orbitals are concentrated, the bond is formed in that direction. This explains directional nature of covalent bond and shape of orbital.
- The molecule will be stable because the bonding electron density is in consideration along the inter nuclear axis and that electron density keeps the two atoms attracted to each other.

  The extent of overlapping will depend on size of atom and nature of orbital.

  p – p > s – p > s – s
- Smaller atoms involve in greater overlapping.

  Cl – Cl > Br – Br

  (p – p) (p – p)

(σ) **Sigma bond**	(π) **Pi BOND**
1) It is a strong covalent bond formed by over lapping along internuclear axis.	It is a weak covalent bond formed by the side wise or lateral overlapping
2) It involves head on (or) end – on – end overlapping.	It involves lateral and sidewise overlapping above and below the axis.
3) The bonding electron density is symmetrical and lies along the axis	Pi electron density lies above and below the axes.
4) Sigma bond is formed by overlapping of any two half filled orbitals	It is formed by the overlapping of p – p or p – d orbitals.

(s - s, s - p, p - p)	
5) It can be formed by pure valence orbitals or hybrid orbitals.	It is formed by only pure valence orbitals.
6) If s orbital is involved in overlapping, the bond formed is always sigma.	If p-orbital is involved in overlapping, it may be sigma or pi
7) The first formed bond between two atoms is always sigma bond. Sigma has Independent existence	It is formed only after the formation of sigma bond. It has no Independent existence
8) It determines the geometry of molecules	It has no role in determining geometry of molecules.
9) One of the two lobes is involved in over lapping	Both the lobes of p - orbital are involved in bond formation
10) Free rotation of orbitals is possible around sigma bond.	Free rotation of orbitals is restricted

All single bonds are sigma bonds

- In double bond, one σ and and one π bonds are present.
- In triple bond, one σ and 2 π bonds are present.

Eg : CH_4 4σ and 0 π
N_2 1σ and 2π
O_2 1σ and 1π

VSEPR Theory:

(Valence shell electron pair repulsion theory)

This was proposed by Gillespe and Nyholm

- It mainly deals with repulsions in between e^-_s and shapes of molecules.

Postulates:

The electron pairs present in valence shell of central atom will be situated around it so that repulsions are minimum.

- The electron pair shared between two atom is called localised (fixed) electron pair and the bond is called localised electron pair bond.
  Order of repulsions in between various Electron pairs:
  Lone pair - lone pair > lone pair - bond pair > bond pair - bond pair
- Lone pair is attracted by one nucleus where as bond pair by two nuclei.

∴ lone pair occupies more spaces and bond pair less space

- In case of bond pairs, triple bond causes more repulsion than double bond and double bond more than single bond
- The bond pair – bond pair repulsion is influenced by EN of central atom (BP – BP repulsion ∝ EN)
- If the central atom contains only bond pairs, the molecule will have regular geometry. If one or more lone pairs are present, it will have irregular geometry
  Thus, shape of molecule depends on extent of mutual repulsions between various electron pairs.
  Eg : $CH_4 \rightarrow$ 4 bond pairs and no lone pairs.
  ∴ Its shape is regular tetrahedral
  In ammonia, there are three bond pairs and one lone pair.

$\therefore$ shape is irregular i.e., pyramidal.

In H_2O, these are two bond pairs and two lone pairs

$\therefore$ shape is irregular i.e., angular.

Due to the presence of lone pairs, bond angles are deviated.

VSEPR theory is useful to predict the shapes of molecules, and type of hybridisation, based on the no of electron pairs present in valence shell of central atom.

Predicting type of hybridisation and The shape of the molecule :

Number of electron pairs in central atom = $\frac{\text{Group number of central atom} + \text{number of bonded pairs}}{2}$

$BeCl_2$	number of e^- pairs =	$\frac{2+2}{2} = 2$	sp	linear
BCl_3	number of e^- pairs =	$\frac{3+3}{2} = 3$	sp^2	Trigonal planar
SO_2	number of e^- pairs =	$\frac{6+0}{2} = 3$	sp^2 (2b.p + 1*l.p*)	Angular
SO_3	number of e^- pairs =	$\frac{6+0}{2} = 3$	sp^2 (3b.p + O *l.p*)	Trigonal planar
NH_3	number of e^- pairs =	$\frac{5+3}{2} = 4$	sp^3 (3b.p + I *l.p*)	Pyramidal
H_3O^+	number of e^- pairs =	$\frac{6+3-1}{2} = 4$	sp^3	Pyramidal

No. of **electron pairs**	**Bond pairs**	**lone pairs**	**Hybridi-sation**	Shape	**Angle**	**Examples**
2	2	-	sp	Linear	180°	$BeCl_2$, CO_2, HCN
3	3	-	sp^2	Trigonal planar	120°	BCl_3,BF_3, SO_2
	2	1	sp^2	Angular	-	SO_2, $SnCl_2$
4	4	-	sp^3	Tetrahedral	109°	CH_4, CCl_4,CF_4
	3	1	sp^3	Pyramidal	107°	NH_3, H_3O^+ (Hydronium ion)
	2	2	sp^3	Angular	-	H_2O, H_2S, Cl_2O, OF_2
5	5	-	sp^3d	Trigonal bipyramidal	90°, 120° 180°	PCl_5, PF_5
	4	1	sp^3d	Distorted tetrahedral	-	SCl_4, SF_4
	3	2	sp^3 d	T	90°, 180°	ClF_3, BrF_3,ICl_3
	2	3	sp^3 d	Linear	180°	XeF_2, ICl_2
6	6	-	sp^3d^2	Octahedral	90°	SF_6
	5	1	$sp^3 d^2$	Distorted octahedral	-	ClF_5, IF_s
	4	2	$sp^3 d^2$	Square planar	90°	XeF_4

7	7	-	$sp^3 d^3$	Pertagonal bipyramidal	72°, 90°	IF_7
	6	1	$sp^3 d^3$	Distorted octahedral	-	XeF_6

CCl_4 number of e⁻ pairs = $\frac{4+4}{2} = 4$ tetrahedral

PCl_5 number of e⁻ pairs = $\frac{5+5}{2} = 5$ sp^3d trigonal bipyramidal

SF_6 number of e⁻ pairs = $\frac{6+6}{2} = 6$ $sp^3 d^2$ octahedral

IF_7 number of e⁻ pairs = $\frac{7+7}{2} = 7$ sp^3d^3 pentagonal bipyramidal

H_2O number of e⁻ pairs = $\frac{6+2}{2} = 4$ (2 b.p + 2 l.p) sp^3 Angular

NH_3 number of e⁻ pairs = $\frac{5+3}{2} = 4$ (3 b.p + 1 l.p) sp^3 Pyramidal

NF_3 number of e⁻ pairs = $\frac{5+3}{4} = 4$ sp^3(3b.p + 1l.p) Pyramidal

PCl_3 number of e⁻ pairs = $\frac{5+3}{2} = 4$ sp^3(3b.p + 1 l.p) Pyramidal

$POCl_3$ number of e⁻ pairs = $\frac{5+3}{2} = 4$ sp^3(4b.p + o l.p) Tetrahedral

$SOCl_2$ number of e⁻ pairs = $\frac{6+2}{2} = 4$ sp^3(3b.p + 1 l.p) Pyramidal

XeF_2 number of e⁻ pairs = $\frac{8+2}{2} = 5$ sp^3d (2b.p + 3 l.p) Linear

XeF_4 number of e⁻ pairs = $\frac{8+4}{2} = 6$ sp^3d^2 (4b.p + 2 l.p) Square planar

XeF_6 number of e⁻ pairs = $\frac{8+6}{2} = 7$ sp^3d^3(6b.p + 1 l.p) distorted octahedral

ClF_3 number of e⁻ pairs = $\frac{7+3}{2} = 5$ sp^3d (3b.p + 2 l.p) T shape

sp^3d (4b.p + 1l.p) Distorted tetrahedral

The above formula to calculate the number of electron pairs is applicable only for simple molecules or ions mentioned above.

It is not applicable for

- Polycentred molecules like C_2H_6, C_2H_4, C_2H_2, etc
- Polymeric substances like diamond (SP^3) graphite (SP^2); polyethene (SP^2); SiC (SP^3),
  It is also not applicable for odd electronic species like NO, NO_2, ClO_2, etc.

Co-ordinate covalent bond (dative bond):

It is proposed by Sidgewick.

- Co-ordinate covalent bond is the bond formed by the sharing of electron pair but the shared pair is contributed by only one atom.
- Thus, in covalent bond both atoms will contribute and share, but in co-ordinate bond, one contributes and both will share
- To form co-ordinate covalent bond, there must be an electron pair donor and electron pair acceptor.

- Covalent bond is denoted by "___" where as co-ordinate bond is denoted by "→" directing from donor to acceptor.
- Co-ordinate bond is semi polar bond
- Formation of co-ordinate bond involves over-lapping between completely filled orbital of donor with vacant orbital of acceptor ∴ Co-ordinate bond is rigid and directional like covalent bond.

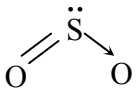
Eg : (i) $H_3\dot{N}\cdot + BF_3 \rightarrow \{H_3N \rightarrow BF_3\}$

(ii) $H_2\dot{O}\cdot + H^+ \rightarrow [H_2O \rightarrow H]^+$ (or) H_3O^+

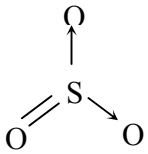
(iii) $Cl^- + AlCl_3 \rightarrow [Cl \rightarrow AlCl_3]^-$ or $AlCl_4^-$

(iv) $H_3\ddot{N}$ $H^+ \rightarrow [H_3N \rightarrow H]^+$ or NH_4^+

(v) SO_2 →



(vi) SO_3 →



Properties of co - ordinate covalent compounds:

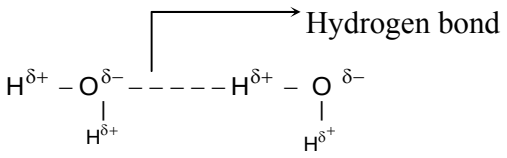
Their properties are almost similar to those of covalent compounds. Some of the properties are in between to those of Ionic and covalent compounds due to semi polar nature of the bond.

1) They are gases or liquids due to weak intermolecular forces.
2) Their melting and boiling points are low due to weak intermolecular forces.
3) They do not conduct electricity due to the absence of ions.
4) They are soluble in non-polar solvents and insoluble in polar solvents like water.
5) Co-ordinate compounds will exhibit Isomerism due to directional nature of bond.
6) The reactions in between co-ordinate compounds are very slow as they involve shuffling of bonds.

HYDROGEN BOND:

Weak electrostatic attraction between hydrogen and more electronegative atom (F, O, N) is called hydrogen bond.

- Due to difference in electronegativity more electronegative atom develops partial negative charge and less electronegative atom develops partial positive charge.
- (H - bond forms) thus, H - bond is formed between partial positively charged H_2 and partial negatively charge electronegative atom.



H - bond is denoted by a broken line (.....).

- It was proposed by Moore and Winmill
- H - bond is the imprisonment of H_2 between two electronegative atoms.

- In H - bond, H is sandwiched between two electronegative atoms.
- In H - bond, H exhibits a valency of 2.
- H - bond is formed by molecules or ions where H is covalently bonded to more electronegative and smaller atoms like F, O, N.
- Identify the molecules which exhibit H - bond in following :
  HF, H_2O, NH_3, HCl, HI, C_2H_5OH,
  $C_2H_5–O–C_2H_5$, $C_2H_5 – NH_2$, $(CH_3)_2$ NH, $(CH_3)_3N$
  Strength of H-bond depends on size and electronegativity of bonding atom.
- Among HF, H_2O, HI; the strongest H - bonds are formed by HF molecules.
- Which of the following is strongest H - bond
  1) H – F …….. H – F
  2) H – OH …… H – OH
  3) H – NH – H ….. NH - H
     |
     H

  Order of strength of hydrogen bond is
  H ..... F > H .....O > H ..... N
- When compared to covalent bond hydrogen bond is weaker, but longer i.e., higher bond length. The bond energy of covalent bond is 400 KJ/ mole and that of H^- bond is 40KJ/mole
  H I Å O (covalent bond)
  H 1.76 Å O (Hydrogen bond).
- Even though N, Cl have same electronegativities; NH_3 forms H-bonds, HCl does not form H - bond because Nitrogen is smaller and chlorine is larger in size.

Types of H bonds :

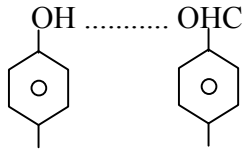
Intermolecular H – bonds :

H - bond is formed between two same molecules or different molecules i.e., H-bond between H of one molecule and more electronegative atom of another molecules

Eg :

H–F$^{\delta-}$……H$^{\delta+}$–F NH_3, RNH_2, R_2NH, ROH

H$^{\delta+}$ – O$^{\delta-}$H … O$^{\delta-}$H Carboxylic acids, Glucose, fructose, Para-nitrophenol, para chlorophenol Parahydroxy benzal dehyde

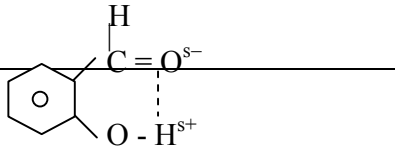


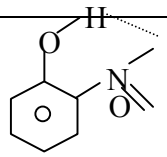
Intramolecular H - bond :

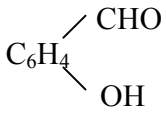
H- bond is formed with in the same molecule i.e., H-bond between δ^+ Hydrogen and δ^- atom both belonging to same molecule

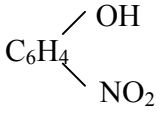
Eg.: Orthohydroxy benzaldehyde (salicylaldehyde) orthohydroxy benzoic acid (salicylic acid) orthonitrophenol, orthoflurophenol, etc.

Salicyaldehyde Orthonitrophenol









Effect of H - bonding: (Intermolecular)

Due to H - bonding,

1) Molecular association increases
2) Melting and boiling points increase
3) Voltaile nature decreases
4) Solubility in water increase
5) Physical state may change

The above effects are observed in case of intermolecular H-bonding but not in the case of intramolecular H-bonding.

Examples :

IV A group hydrides.	V A group Hydrides
CH_4	NH_3
SiH_4	PH_3
GeH_4	AsH_3
SnH_4	SbH_3
PbH_4	BiH_3

Though, molecular weight of NH_3 is less, its BP is much higher than those of PH_3 and ASH_3 because of H - bonding.

VI A group hydrides	VII A group hydrides
H_2O (High BP)	HF (High BP)
H_2S	HCl
H_2Se	HBr
H_2Te	HI
H_2Po	

Though molecular weight of H_2O is least it's boiling point is highest than other hydrides of group due to H-bonding Though molecular weight of HF is least, its boiling point is highest than all others due to H-bonding

- Two ice cubes can be pressed over each other due to formation of H- bond.
- H_2O is liquid while H_2S is gas due to H- bonding in H_2O. Each water molecule can form four H - bonds on an average.
- Certain covalent substances like glucose, fructose, sugar, urea, alcohol, amines, carboxylic acids are soluble in water due to H – bonding.
- Orthonitrophenol is more volatile because it forms intramolecular H - bonds.
- Paranitrophenol is less volatile because it forms intermolecular H- bonds.
- Orthohydroxy benzaldehyde (salicylaldehyde) is more volatile and forms intra-molecular H-bonds while parahydroxy benzaldehyde is less volatile because of intermolecular H⁻ bonding.

- Certain substances like acetic acid, benzoic acid hydroflouric acid will exist in dimeric form due to H-bonding.
- Generally, H bonds are formed in solid and liquid state. But, HF can form H-bonds even in vapour state.

Though HF forms strongest H bonds and has high molecular weight than that of H_2O, the boiling point of HF is very less when compared to boiling point of H_2O. It is due to

1) H_2O forms double the number of H - bonds than HF.
2) HF can form H - bonds even in vapour state and exists as clusters $[(HF)_6]$ in vapour state.

Thus, it is not necessary to break all H - bonds in HF to vapourise it.

POLARITY - DIPOLE MOMENT:

If covalent bonds are present between same atoms, the electron pairs are equally shared in between them. In such molecules, positive or negative charges are not developed on any atom. Such covalent bonds are called non-polar covalent bonds and the molecules may be called **non-polar molecules.**

Eg. H_2, N_2, O_2, F_2, Cl_2, etc.

- If covalent bonds are present between dif. atoms, the bonded e^- pair is unequally shared in between them. More electronegative atom shares more and less electron negative atom shares less As a result, more electronegative develops negative charge; and less electronegative atom develops positive charge. Such covalent bonds are called **Polar covalent bonds** and the molecules are called polar molecules and the phenomenon is called polarity.

The above polar molecules are called dipoles. Magnitude of polarity will depend on EN difference between bonded atoms.

HF > HCl > HBr > HI

O - H > S - H > Se - H > Te - H

O - H > N - H > S - H

(EN difference decrease s, polarity decreases)

N - Cl < P - Cl < As - Cl < Bi - Cl

(EN difference increases, polarity increases)

I - F > Cl - F > I - Cl > Br - Cl

(EN difference decreases, polarity decreases)

Dipole moment :

The magnitude of polarity in the molecule is expressed in terms of dipole moment value.

Dipole moment is defined as the product of charge and the distance between the charges.

$\mu = e \times d$

$\mu = \delta \times l$

Where $\mu \rightarrow$ dipole moment

$e, \delta \rightarrow$ charge

$d, l \rightarrow$ distance (bond length)

Units of dipole moment : Debyes

1 Debye = 10^{-18} e.s.u cm

1 Debye = 3.33×10^{-30} coloumbmetre

The dipole moment of each bond is called bond - dipole or bond - moment the direction of the bond moment ($\rightarrow$) is from less EN to more EN atom.

- Dipole moment is a vector quantity. $\therefore$ the net dipole moment of molecule is the vector sum of bond dipoles, but it is not simply the sum of bond - dipoles
- The net dipole moment of the molecule depends on

1) Polarity of bonds
2) Shapes of the molecules.

- If only bond - pairs are present the molecule has regular shape and its dipole moment will be zero due to mutual cancellation of the bond moments.

  Eg : All linear molecules are non polar, $\mu = 0$

  $BeCl_2$, BeF_2, CO_2

  All trigonal molecules are non - polar, $\mu = 0$

  Eg : BF_3, PCl_3, BBr_3, SO_3, BI_3, etc
- All regular tetrahedral molecules are non-polar, $\mu = 0$.

  Eg : CCl_4, CF_4, $SiCl_4$, SiF_4, CH_4, $SnCl_4$
- The molecule in which central atom contains one or more lone pairs will have irregular geometry and such molecules are polar and they have net dipole moment value.

  Eg : H_2O, H_2S, SO_2, $SnCl_2$

  These are angular and $\mu \neq 0$
- SCl_4, SF_4, $SeCl_4$, are distorted tetrahedral $\mu \neq 0$ and are polar.
- Thus, the molecule with polar bonds may be polar or non-polar as discussed above.
- Among the ortho, meta, para Isomers of a given compound μ ortho > μ meta > μ para
- In cis and trans Isomers of a compound $\mu_{cis} > \mu_{trans}$
- The shape of AB_4 molecule for which observed $\mu = 0$ is tetrahedral.

APPLICATIONS OF DIPOLE MOMENT:

1) The shape of the molecule and hybridisation of central atom can be predicted.

   $\mu_{CO_2} = 0$ linear (sp)

   $\mu_{SO_3} = 0$ trigonal planar (sp^2)

   $\mu_{CCl_4} = 0$ tetrahedral (sp^3)

   $\mu_{SO_2} \neq 0$ Angular (sp^2)

   $\mu_{H_2O} \neq 0$ Angular (sp^3)

   $\mu_{SnCl_2} \neq 0$ Angular(sp^2)

   $\mu_{NH_3} \neq 0$ Pyramidal (sp^3)

2) Cis and trans Isomers of a compound can be distinguished.

   $\mu_{cis} > \mu_{trans}$

3) Ortho, meta, para Isomeras of a compound can be distinguished

   $\mu_{ortho} > \mu_{meta} > \mu_{para}$

4) % Ionic character can be calculated. Greater the EN difference, greater is the dipole moment value and greater is the ionic character.

   % Ionic Character = $\frac{\mu_{obs}}{\mu_{cal}} \times 100$

Examples:

1. The dipole moment of HCl is 1.03 debyes. If the bond length is 1.28 Å
   Calculate % Ionic character.

   $\mu_{cal} = e \times d$

   $= 4.8 \times 10^{-10} \times 1.28 \times 10^{-8}$

   $= 4.8 \times 1.28 \times 10^{-18}$

   $= 4.8 \times 1.28$ Debyes

   % Ionic character = $\frac{1.03 \times 100}{4.8 \times 1.285} = 16.8$ %

2. Dipole moment of. HF is 1.92 Debyes If bond length of HF is 0.9 Å. Calculate its Ionic character.

   $\mu_{cal} = 4.8 \times 10^{-18} \times 0.9$ Å

   $= 4.8 \times 0.9$ debyes

   % Ionic character $= \frac{1.92}{4.8 \times 0.9} \times \frac{10^{-18} \times 100}{10^{-18}}$

   $= \frac{192}{48 \times 9} \times 100 = 44\%$

$\mu_{obs} = 2 \times$ bond moment $\times \cos \frac{\theta}{2}$

3. The dipole moment of H_2S molecule is 0.95 debyes. If the bond angle is 92^0. Calculate the bond moment of S - H bond
   ($\cos 46^0 = 0.65$)

   $\mu_{obs} = 2 \times$ bond moment $\times \cos \frac{\theta}{2}$

   $0.95 = 2 \times x \times \cos 46$

   $0.95 = 2 \times x \times 0.65$

   $2x = \frac{95}{65} = \frac{19}{13}$

   $2x = 1.46$

   $x = 0.73$

Though EN difference between N and F is greater than that of between N and H Even though, both NH_3 and NF_3 are pyramidal $\mu_{NH_3} > \mu_{NF_3}$

In NH_3, the lone pair contributes in the same direction as those of bond dipoles where as in NF_3 lone pair contributes in opposite direction as those of bond – dipoles



In case of AB_2 type tri - atomic molecules μ value increases with decrease in the bond angle

METALLIC BOND:

The force of attraction that binds the metal atoms in metallic crystal is called metallic bond. The nature of metallic bonding is explained by following three theories.

1) Free e^- theory
2) Valence bond theory
3) Molecular orbital theory.

Free electron theory:

(Electron pool theory or electron gas theory)

- This was proposed by Orude and Lorance.
- All metal atoms loose their valence e^- in metallic crystal.
- All these valence electrons together will form an electron pool or electron gas.
- The force of attraction between positively charged metal ions and negative electron pool is called metallic bond.
- These deloclised e^-s move freely into the vacant orbitals of all positively charged ions. Thus, metal is imagined to be positively charged ions immersed in a sea of mobile electrons.

The strength of metallic bond will depend on (1) size of the atom (2) number of participating e^-s

- Smaller atoms with more number of valence e^-s will form stronger metallic bonds.
- In case of stronger metallic bonds, metals are hard with high melting and boiling points.
- Metallic bond is non-directional as it involves delocalised electrons.
- Though this theory could explain conductivity, metallic luster and some other properties, it fails to explain the differences in properties between various metals.

VALENCE BOND THEORY:

This was proposed by pauling.

- Acc. to this theory, metallic bond is similar to that of covalent bond.
- A metal atom is bonded to its neighbouring atoms by the sharing of e^- pairs. But, these shared pairs are not localised because they move freely into vacant orbitals of metal atoms.
- In metallic crystal, each metal atom is surrounded by numerous metal atoms. The central atom can form a bond with any one of metal atom and it results in various resonance structures.
- Because of resonance, the metallic crystal is stable and metallic bonds are stronger (metal atom).

BOND PARAMETERS:

Covalent bond is characterised by the following:

1) bond length 2) bond angle 3) bond energy

Bond length : It is the average distance between two bonded atoms it is expressed in Angstrom units (Å).

Bond length depends on

i) Size of atom: with increase in size of bonded atom, bond-length increases.
$H - F < H - Cl < H - Br < H - I$

ii) Bond order: The number of bonds between two atoms is called bond order. With increase in bond-order, bond length value decreases

	$1.54\,A^0$	$1.34\,A^0$	$1.2\,A^0$
	$C - C$	$C = C$	$C \equiv C$
B.O.:	1	2	3

iii) **S-character:-** With increase in S-character size of orbital decreases and bond length decreases.

$$H - \underset{\underset{S - sp^3}{|}}{C} > H - \underset{S - sp^2}{\underset{|}{C}} = > H - C \equiv \underset{S - sp}{}$$

iv) With increase in polarity, bond length decreases.

H - F < H - Cl < H - Br < H - I

v) **Resonance:** Because of resonance, the bond lengths of different bonds will become identical. Generally, the bond length will be in between that of single bond length value and double bond length value.

Eg.: In O_3, bond length between two oxygens is 1.28 Å which is in between $\overset{1.48A^0}{O \rightarrow O}$ and $\overset{1.2A^0}{O = O}$.

BOND ANGLE:-

It is the angle between the two adjacent bonded atoms. Bond angle depends on

i) Nature of hybridisation : sp - 180^0, sp^2 - 120^0, sp^3 - 109^0.

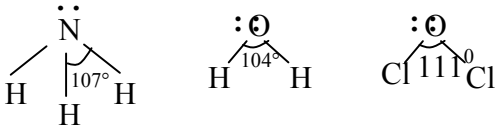
ii) S-character: With increase in S-character bond angle increases.

$sp \rightarrow 180^0$ ↑

↑ S-charcter sp^2 - 120^0

↑ bond angle sp^3 - 109^0.

iii) Repulsions in between the electron pairs : Due to repulsions in between lone pairs, bond angle decreases. If the repulsions between bond pairs are more, bond angle increases.



iv) Electrongegativity:- With decrease in EN of central atom, the bond angle decreases.

EN ↓	H_2O	104°	NH_3	107°
	H_2S	92°	PH_3	93°
BA ↓s	H_2Se	91°	ASH_3	91° 30’
	H_2Te	90°	SbH_3	91°

If the EN of bonded atoms decreases, bond angle increases

$OF_2 \rightarrow 104°$ $Cl_2O \rightarrow 111°$

BOND ENERGY:-

The amount of energy released when one mole of bonds are formed (or) the amount of energy absorbed to break one mole of bond.

Bond energy usually refers to bond dissociation energy.

$H + H \rightarrow H – H$; 104 kcal

$H – H \rightarrow H + H$; –104 kcal

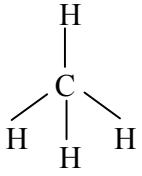
In case of polyatomic molecule, the bond energy of particular bond is the average of sum of all bond energies.

$CH_4 \rightarrow CH_3 + H$; x_1

$CH_3 \rightarrow CH_2 + H$; x_2

$CH_2 \rightarrow CH + H$; x_3

$CH \rightarrow C + H$; x_4



Bond energy of C - H bond = $(x_1 + x_2 + x_3 + x_4) / 4$

1. Bond energy of CH_4 is 360 k.cal/mole and that of C_2H_6 is 620 k.cal/mole. Calculate the bond dissociation energy of C – C bond

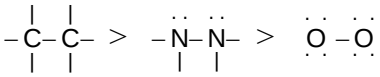
   Bond energy of C - H bond = 360 / 4 = 90 k.cal

   In Ethane there are six C - H bonds and one C - C bonds. $620 = 6 \times 90 - x$

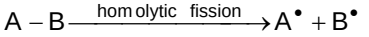
x = 80 k.cal

Factors influencing bond energy :

1) **Size of bonded atom:**
   with increase in size of bonded atom, bond energy decreases.
   C – H > Si – H > Ge – H > Sn – H > Pb – H
   C–C > Si – Si > Ge – Ge > Sn – Sn > Pb – Pb
2) **Bond order:** With increase in the bond order, bond energy increases.
3) **Presence of lone pairs:** With increase in the number of lone pairs, bond energy decreases.



4) **P-character:** With increase in the
   P-character of orbital, the extent of overlapping increases and bond energy increases.
   i) $sp^3 - sp^3 > sp^2 - sp^2 > sp - sp$ $\quad p - p > s - p > s - s$
5) **Polarity:** With increase in polarity, bond energy increases.
   H - F > H - Cl > H - Br > H - I
6) **Resonance:** Resonance leads to the stability of bonds and increases the bond energy.
7) **Type of bond fission:** Bond can be fissioned by homolytic or heterolytic way. Energy required for homolytic fission is less than heterolytic fission.





- If the bond energy is more, the molecule is more stable and reactivity is less.
- Even though EN of nitrogen is more N_2 is less reactive due to greater bond energy.

Predicting the type of bonds:-

- The bond between two electronegative atoms is covalent bond.
- The bond between two electropositive elements is metallic bond.
- The bond between electropositive and electronegative element is ionic bond.

	Ionic	Covalent	Co-ordinate covalent
NaCl	✓		
HCl		✓	
NaOH	✓	✓	
NaCN	✓	✓	
HCN		✓	
$CH_3 - NH_2$		✓	
NH_3		✓	
NH_4^+		✓	✓
H_2O		✓	
H_3O^+		✓	✓
NH_4Cl	✓	✓	✓
SO_2		✓	✓
SO_3		✓	✓
SO_4^{2-}	✓	✓	✓
$CuSO_4$	✓	✓	✓
$CuSO_4.5H_2O$	✓	✓	✓

$Ni(CO)_4$		✓	✓
$Fe(CO)_5$		✓	✓
$K_4[Fe(CN)_6]$	✓	✓	✓

Number of sigma bonds = Atomicity - 1

Atomicity → number of atoms in a compound

Eg.: CO_2 $\sigma = 3 - 1 = 2$ $\pi = 2$

CH_4 $\sigma = 5 - 1 = 4$ $\pi = 0$

C_2H_6 $\sigma = 8 - 1 = 7$ $\pi = 0$

C_2H_4 $\sigma = 6 - 1 = 5$ $\pi = 1$

C_2H_2 $\sigma = 4 - 1 = 3$ $\pi = 2$

HCN $\sigma = 3 - 1 = 2$ $\pi = 2$

MOLECULAR ORBITAL THEORY

- **Molecular orbital theory or Hund-Mulliken theory**- According to this theory the atomic orbitals combine to form the molecular orbitals. The number of molecular orbitals formed is equal to the number of atomic orbitals involved and they belong to the molecule.
- The molecular orbitals are formed by LCAO method (linear combination of atomic orbitals) *i.e.* by addition or subtraction of wave functions of individual atoms thus

  $\Psi_{MO} = \Psi_A + \Psi_B$

  $\Psi_b = \Psi_A + \Psi_B$

  $\Psi_a = \Psi_A - \Psi_B$

  ψ_b = bonding molecular orbital

  ψ_a = Anti bonding molecular orbital
- the number of molecular orbitals resulting are equal to number of atomic orbitals combining.
- The order of energies of molecular orbitals is bonding orbitals < Non-bonding orbitals < Anti-bonding orbitals.
- Molecular orbitals with lower energy than atomic orbitals are bonding orbitals and those with higher energy is anti-bonding and which are not involved in bonding are called non-bonding orbitals.

- Molecular orbital of lower energy is known as bonding molecular orbital and of higher energy is known as antibonding molecular orbital.
- Molecular orbitals are characterised by a set of quantum numbers.
- Aufbau rule, Pauli's exclusion principle and Hund's rule are applicable to molecular orbitals, during the filling electrons
- Their shape is governed by the shape of atomic orbitals

The increasing order of relative energies of M.O having less than or **equal to 14 electrons.**

$\sigma 1s < \sigma^* 1s < 2s < {}^*2s < 2p_z < \sigma \quad \pi$

$\pi 2py < \sigma 2p_x < {}^*2p_z = {}^*2p_y < {}^*2p_x \quad \pi \quad \sigma$

for more than 14 electrons

$\sigma 1s < \sigma^* 1s < 2s < {}^*2s < 2p_x \; \sigma \quad \sigma$

$< \left[\pi 2p_z = \pi 2p_y\right]$

$< \left[\pi^* 2p_z = \pi^* 2p_y\right] < {}^*2p_x \quad \sigma$

Atomic and Molecular Orbitals Main differences

Atomic Orbitals	Molecular orbitals
1) They belong to one specific atom only	1) They belong to all the atoms in a molecule
2) They are the internal characteristic of an atom .	2) They result when atomic orbital of similar energies combine.
3) They have simple shapes of geometries .	3) They have complex shapes
4) The atomic orbitals are named as s,p,d,f….etc	4) The molecular orbitals are named as σ, π, δ .etc.
5) The stabilities of these orbitals are less than bonding and more than the antibonding	5) The stabilities of these orbitals are either more or less than the atomic orbitals orbitals

Difference between σ and π MO's

	σ - molecular orbital	π- molecular orbital
1)	Formed by the end on overlap along the internuclear axis	1) Formed by the sidewise overlap erpendicular to inter nuclear axis
2)	Overlapped region is very large	2) Over lapped region is small
3)	Rotation about the internuclear axis is symmetrical	3) Rotation about the inter nuclear axis is. unsymmetrical
4)	Strong bonds are favoured	4) Weak bonds are favoured

STABILITY OF MOLECULES :-

If N_b is the number of electrons occupying bonding orbitals and N_a the number of antibonding orbitals, then

(i) The molecule is stable if N_b is grater than N_a

(ii) The molecule is unstable if N_b is less than N_a.

Note : $KK = \sigma 1s^2 . \sigma^* 1s^2$

Electronic configuration /Bond order of simple diatomic molecules

The electronic configuration and the bond order in case of simple diatomic molecules can be obtained by filling the molecular orbitals by applying Aufbau principle and Hunds rule etc.

- **BOND ORDER:** The relative stability of a molecule can be determined on the basis of bond order. It is defined as the number of covalent bonds in a molecule. It is equal to **one half of the difference between the number of electrons in the bonding and antibonding molecular orbitals.**

Bond order = $\frac{1}{2}$ [Number of bonding electrons - Number of antibonding electrons]

or $= \frac{N_b - N_a}{2}$

The bond orders of 1,2 or 3 correspond to single, double or triple bond. But bond order may be fractional in some cases.

The magnetic properties of molecules can also be ascertained

- **Bonding in some diatomic molecules and ions**
- **Hydrogen molecule -**

Total number of electrons = 2, filling in molecular orbitals we have $\sigma_{1s}^2 < \sigma_{1s}^{*0}$

Bond order = $\frac{(N_b - N_a)}{2} = \frac{2-0}{2} = 1$

Hence there is a single bond between two hydrogen atoms and due to absence of unpaired electrons it is **diamagnetic**

- **Helium molecule (He_2) -**

The total number of electrons =4 and filling in molecular orbitals we have $\sigma_{1s}^2 < \sigma_{1s}^{*2}$

Bond order = $\frac{(N_b - N_a)}{2} = \frac{2-2}{2} = 0$

Hence He_2 molecule **can not exist**

- **Nitrogen molecule (N_2) -**

The total number of electrons =14 and filling in molecular orbitals we have

$$\sigma_{1s}^2 \ \sigma_{1s}^{*2} \ \sigma_{2s}^2 \ {}^{*2}_{2s} \left\{ \begin{matrix} \sigma_{2Pz}^2 \\ \pi_{2Py}^2 \end{matrix} \right\} \ {}^{2}_{2Px} \quad \sigma$$

Bond order = $\frac{(N_b - N_a)}{2} = \frac{10-4}{2} = 3$

It is **diamagnetic**

- **Oxygen molecule (O_2) -**

Total number of electrons =16 and electronic configuration is

$\sigma_{1s}^2\ \sigma_{1s}^{*2}\ \sigma_{2s}^2\ \ ^{*2}_{2s}\ \ ^{2}_{2Px}\left\{\begin{matrix}\sigma\ ^{2}_{2Pz}\\ \pi^2_{2Py}\end{matrix}\right\}\left\{\begin{matrix}^{*1}_{2Pz}\pi\\ \pi^{*1}_{2Py}\end{matrix}\right\}\ \ ^{*}_{2Px}\quad \pi \qquad \sigma$

Bond order = $\frac{(N_b - N_a)}{2} = \frac{10-6}{2} = 2$

As shown by electronic configuration the O_2 molecule contains two unpaired electrons, hence it is **paramagnetic** in nature

- **O_2^+ ion -**

  Total number of electrons (16 - 1) = 15,

  Electronic configuration $\sigma_{1s}^2\ \sigma_{1s}^{*2}\ \sigma_{2s}^2\ \ ^{*2}_{2s}\ \ ^{2}_{2Px}\left\{\begin{matrix}\sigma\ ^{2}_{2Pz}\\ \pi^2_{2Py}\end{matrix}\right\}\left\{\begin{matrix}^{*1}_{2Pz}\pi\\ \pi^{*}_{2Py}\end{matrix}\right\}\ \ ^{*}_{2Px}\quad \pi \qquad \sigma$

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

It is paramagnetic

- **O_2^- (Super oxide ion):**

  Total number of electrons (16 +1) = 17. Electronic fonguration

$\sigma_{1s}^2\ \sigma_{1s}^{*2}\ \sigma_{2s}^2\ \ ^{*2}_{2s}\ \ ^{2}_{2Px}\left\{\begin{matrix}\sigma\ ^{2}_{2Pz}\\ \pi^2_{2Py}\end{matrix}\right\}\left\{\begin{matrix}^{*2}_{2Pz}\pi\\ \pi^{*1}_{2Py}\end{matrix}\right\}\ \ ^{*}_{2Px}\quad \pi \qquad \sigma$

  Bond order = $\frac{(Nb - Na)}{2} = \frac{10-7}{2} = 1.5$

  It is **paramagnetic**

- **Peroxide ion $\left(\mathbf{O_2^{2-}}\right)$** - Total number of electrons (16 + 2) =18. The electronic configuration is $\sigma_{1s}^2\ \sigma_{1s}^{*2}\ \sigma_{2s}^2\ \ ^{*2}_{2s}\ \ ^{2}_{2Px}\left\{\begin{matrix}\sigma\ ^{2}_{2Pz}\\ \pi^2_{2Py}\end{matrix}\right\}\left\{\begin{matrix}^{*2}_{2Pz}\pi\\ \pi^{*2}_{2Py}\end{matrix}\right\}\ \ ^{*}_{2Px}\quad \pi \qquad \sigma$

  Bond order = $\frac{10-8}{2} = 1$

  It is **diamagnetic**

- $[B_2]$ *no of electrons* $=10$

  The electronic configuration is $\sigma 1s^2\ \sigma^* 1s^2\ \ 2s^2\ \ ^*\sigma s^2\ \ \sigma p^1{}_y = \ 2p^1{}_z\ \pi \qquad \pi$

  it has 2 paired electrons . Hence **paramagnetic**

- **FORMAL CHARGE.**

Formal charge is a factor based on a pure covalent bond formed by the sharing of electron pairs equally by neighbouring atoms . Formal charge may be regarded as the charge that an atom in a molecule would have if all the atoms had the same electronegativity. It may or may not approximate the real ionic charge. In case of a polyatomic ions, the net charge is possessed the real ion as a whole and not by an particular atom. It is, however, feasible to assign a formal charge on an atom in a polyatomic molecule or ion.

Where $Q_f = [N_A - N_M] = [N_A - N_{LP} \ - 1/2 N_{BP}]$

N_A= number of electrons in the valence shell in the free atom

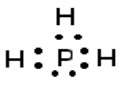
N_M= number of electrons belonging to the atom in the molecule

N_{LP} = number of electrons in unshared pairs, i.e. number of electrons in lone pairs

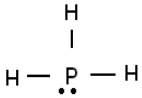
N_{BP} = number of electrons in bond pairs, respectively.

Q_f = Formal charge

Formal charge of P :



(OR)



$$Q_f = [N_A - N_M] = [N_A - N_{LP} - 1/2\ N_{BP}] = \{5 - 2 - 1/2\ (6)\} = (5 - 5) = 0$$

Formal charge of H :

$$Q_f = [N_A - N_M] = [N_A - N_{LP} - 1/2\ N_{BP}] = \{5 - 2 - 1/2\ (6)\} = (5 - 5) = 0$$