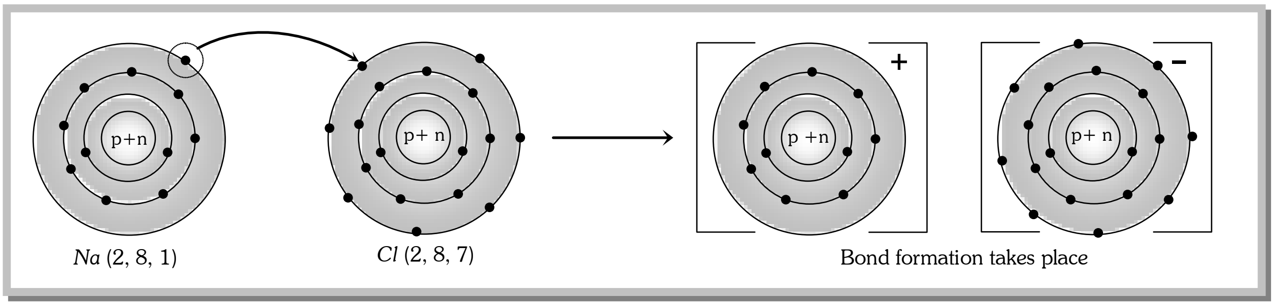
CHEMICAL BONDING AND MOLECULAR STRUCTURE

Atoms of different elements *excepting* noble gases donot have complete octet so they combine with other atoms to form chemical bond. *The force which holds the atoms or ions together within the molecule is called a* ***chemical bond*** and the process of their combination is called ***Chemical Bonding***.

Chemical bonding depends on the valency of atoms. Valency was termed as the number of chemical bonds formed by an atom in a molecule or number of electrons present in outermost shell *i.e.*, valence electrons. Valence electrons actually involved in bond formation are called bonding electrons. The remaining valence electrons still available for bond formation are referred to as non-bonding electrons.



Cause and Modes of chemical combination.

Chemical combination takes place due to following reasons.

(1) *Chemical bonding takes place to acquire a state of minimum energy and maximum stability.*

(2) *By formation of chemical bond, atoms convert into molecule to acquire stable configuration of the nearest noble gas.*

Modes : Chemical bonding can occur in the following manner.

Transfer of electrons from one atom to another	Ionic bond
Mutual sharing of electrons between the atoms	Covalent bond
Mutual sharing of electrons provided entirely by one of the atoms	Co-ordination bond

Electrovalent bond.

When *a bond is formed by complete transfer of electrons from one atom to another* so as to complete their outermost orbits by acquiring 8 electrons (*i.e.,* octet) or 2 electrons (*i.e.,* duplet) in case of hydrogen, helium etc. and hence acquire the stable nearest noble gas configuration, the bond formed is called **ionic bond, electrovalent bond or polar bond**. Compounds containing ionic bond are called **ionic, electrovalent** or **polar compounds.**

Example : $\dot{Na} + \cdot\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}: \rightarrow [Na]^+ \left[:\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}:\right]^-$ or Na^+Cl^-

Some other examples are: $MgCl_2$, $CaCl_2$, MgO, Na_2S, CaH_2, AlF_3, NaH, KH, K_2O, KI, $RbCl$, $NaBr$, CaH_2 etc.

(1) Conditions for formation of electrovalent bond

(i) *Number of valency electrons* **:** The atom which changes into cation (+ ive ion) should possess 1, 2 or 3 valency electrons. The other atom which changes into anion (– ive ion) should possess 5, 6 or 7 electrons in the valency shell.

(ii) *Electronegativity difference* **:** A high difference of electronegativity (about 2) of the two atoms is necessary for the formation of an electrovalent bond. *Electrovalent bond is not possible between similar atoms.*

(iii) *Small decrease in energy* **:** *There must be overall decrease in energy i.e., energy must be released. For this an atom should have low value of* ***Ionisation potential*** *and the other atom should have high value of* ***electron affinity****.*

(iv) *Lattice energy* **:** *Higher the lattice energy, greater will be the ease of forming an ionic compound. The amount of energy released when free ions combine together to form one mole of a crystal is called* ***lattice energy (U).***

$$\text{Magnitude of lattice energy} \propto \frac{\text{Charge of ion}}{\text{size of ion}}$$

$$A^+(g) + B^-(g) \longrightarrow AB(s) + U$$

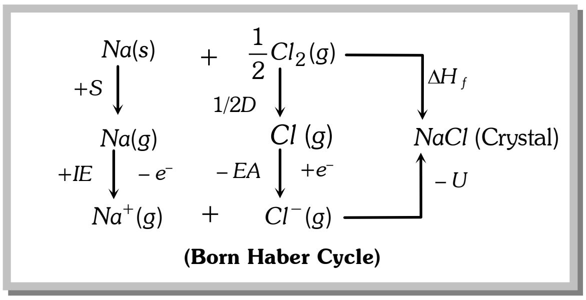
Determination of lattice energy (Born Haber cycle)

When a chemical bond is formed between two atoms (or ions), the potential energy of the system constituting the two atoms or ions decreases. If there is no fall in potential energy of the system, no bonding is possible, the energy changes involved in the formation of ionic compounds from their constituent elements can be studied with the help of a thermochemical cycle called **Born Haber cycle.**

Example : The formation of 1 mole of $NaCl$ from sodium and chlorine involves following steps :

Step I : Conversion of metallic sodium into gaseous sodium atoms: $\underset{1\,mole}{Na(s)} + S \rightarrow Na(g)$, where S= sublimation energy *i.e.*, the energy required for the conversion of one mole of metallic sodium into gaseous sodium atoms.

Step II : Dissociation of chlorine molecules into chlorine atoms : $Cl_2(g) + D \rightarrow 2Cl(g)$, where D = Dissociation energy of Cl_2 so the energy required for the formation of one mole of gaseous chlorine atoms $= D/2$.



(Born Haber Cycle)

Step III: Conversion of gaseous sodium atoms into sodium ions : $\underset{1\,mole}{Na(g)} + IE \rightarrow Na^+(g) + e^-$, where IE = Ionisation energy of sodium.

Step IV: Conversion of gaseous chlorine atoms into chloride ions : $\underset{1\,mole}{Cl(g)} + e^- \rightarrow Cl^-(g) + EA$, where EA = Electron affinity of chlorine.

Step V : Combination of gaseous sodium and chloride ions to form solid sodium chloride crystal.

$Na^+(g) + Cl^-(g) \rightarrow \underset{1\,mole}{NaCl(s)} + U$, where U = lattice energy of $NaCl$

The overall change may be represented as : $Na(s) + \frac{1}{2}Cl_2(g) \rightarrow NaCl(s), \Delta H_f$, where ΔH_f is the heat of formation for 1 mole of $NaCl(s)$.

According to Hess's law of constant heat summation, heat of formation of one mole of $NaCl$ should be same whether it takes place directly in one step or through a number of steps. Thus,

$$\boxed{\Delta H_f = S + \frac{1}{2}D + IE + EA + U}$$

(2) **Types of ions**

The following types of ions are encountered :

(i) *Ions with inert gas configuration* : The atoms of the representative elements of group I, II and III by complete loss of their valency electrons and the elements of group V, VI, and VII by gaining 3,2 and 1 electrons respectively form ions either with ns^2 configuration or ns^2p^6 configuration.

(a) *Ions with $1s^2$ (He) configuration* **:** H^-, Li^+, Be^{2+} etc. The formation of Li^+ and Be^{2+} is difficult due to their small size and high ionisation *potential.*

(b) *Ions with ns^2p^6 configuration* **:** More than three electrons are hardly lost or gained in the ion formation

Cations : Na^+, Ca^{2+}, Al^{3+} etc.

Anions : Cl^-, O^{2-}, N^{3-}, etc.

(ii) *Ions with pseudo inert gas configuration* **:** The Zn^{2+} ; ion is formed when zinc atom loses its outer 4s electrons. The outer shell configuration of Zn^{2+} ions is $3s^2 3p^6 3d^{10}$. The $ns^2np^6nd^{10}$ outer shell configuration is often called pseudo noble gas configuration which is considered as stable one.

Examples: $Zn^{2+}, Cd^{2+}, Hg^{2+}, Cu^+ Ag^+, Au^+, Ga^{3+}$ etc

(iii) *Exceptional configurations* **:** Many *d*- and *f* block elements produce ions with configurations different than the above two. Ions like Fe^{3+}, Mn^{2+}, etc., attain a stable configuration half filled *d*- orbitals

Fe^{3+} $3s^2 3p^6 3d^5$; Mn^{2+} $3s^2 3p^6 3d^5$

Examples of other configurations are many.

Ti^{2+} $(3s^2 3p^6 3d^2)$; V^{2+} $(3s^2 3p^6 3d^3)$

Cr^{2+} $(3s^2 3p^6 3d^4)$; Fe^{2+} $(3s^2 3p^6 3d^6)$

However, such ions are comparatively less stable

(iv) *Ions with ns^2 configuration* **:** Heavier members of groups III, IV and V lose *p*-electrons only to form ions with ns^2 configuration. $Tl^+, Sn^{2+}, Pb^{2+}, Bi^{3+}$ are the examples of this type. These are stable ions.

(v) *Polyatomic ions* **:** The ions which are composed of more than one atom are called polyatomic ions. These ions move as such in chemical reactions. Some common polyatomic ions are

NH_4^+ (Ammonium);	NO_3^- (Nitrate)
PO_4^{3-} (phosphate);	SO_4^{2-} (Sulphate)
CO_3^{2-} (Carbonate) ;	SO_3^{2-} (Sulphite), etc.

(vi) *Polyhalide ions* : Halogens or interhalogens combine with halide ions to form polyhalide ions. I_3^-, ICl_4^-, ICl_2^- etc. Fluorine due to highest electronegativity and absence of d-oribitals does not form polyhalide ions.

The atoms within the polyatomic ions are held to each other by covalent bonds.

The electro valencies of an ion (any type) is equal to the number of charges present on it.

(3) **Method of writing formula of an ionic compound**

In order to write the formula of an ionic compound which is made up of two ions (simple or polyatomic) having electrovalencies x and y respectively, the following points are followed :

(i) Write the symbols of the ions side by side in such a way that positive ion is at the left and negative ion at the right as AB.

(ii) Write their electrovalencies in figures on the top of each symbol as $A^x B^y$

(iii) Divide their valencies by H.C.F

(iv) Now apply criss cross rule as $\begin{array}{ccc} x & \times & y \\ A & & B \end{array}$, i.e., formula $A_y B_x$

Examples :

Name of compound	*Exchange of valencies*	*Formula*	*Name of compound*	*Exchange of valencies*	*Formula*
Calcium chloride	$\begin{array}{ccc} 2 & \times & 1 \\ Ca & & Cl \end{array}$	$CaCl_2$	**Aluminium oxide**	$\begin{array}{ccc} 3 & \times & 2 \\ Al & & O \end{array}$	Al_2O_3
Potassium phosphate	$\begin{array}{ccc} 1 & \times & 3 \\ K & & PO_4 \end{array}$	K_3PO_4	**Magnesium nitride**	$\begin{array}{ccc} 2 & \times & 3 \\ Mg & & N \end{array}$	Mg_3N_2
Calcium oxide	$\overset{2}{Ca}\overset{2}{O}$ **or** $\begin{array}{ccc} 1 & \times & 1 \\ Ca & & O \end{array}$	CaO	**Ammonium sulphate**	$\begin{array}{ccc} 1 & \times & 2 \\ NH_4 & & SO_4 \end{array}$	$(NH_4)_2SO_4$

(4) Difference between atoms and ions

The following are the points of difference between atoms and ions.

Atoms	*Ions*
1. Atoms are perfectly neutral in nature, i.e., number of protons equal to number of electrons. Na (protons 11, electrons 11), Cl (Protons – 17, electrons –17)	**Ions are charged particles, cations are positively charged, i.e., number of protons more than the number of electrons. Anions are negatively charged, i.e., number of protons less than the number of electrons.** **Na^+ (protons 11, electrons 10), Cl^- (protons 17, electrons 18)**
2. Except noble gases, atoms have less than 8 electrons in the outermost orbit **Na 2,8,1; Ca 2,8,8,2** **Cl 2,8,7; S 2,8,6**	**Ions have generally 8 electrons in the outermost orbit, i.e., ns^2np^6 configuration.** **Na^+ 2,8; Cl^- 2,8,8** **Ca^{2+} 2,8,8**
3. Chemical activity is due to loss or gain or sharing of electrons as to acquire noble gas configuration	**The chemical activity is due to the charge on the ion. Oppositely charged ions are held together by electrostatic forces**

(5) Characteristics of ionic compounds

(i) *Physical state* **:** Electrovalent compounds are generally crystalline is nature. The constituent ions are arranged in a regular way in their lattice. These are hard due to strong forces of attraction between oppositely charged ions which keep them in their fixed positions.

(ii) *Melting and boiling points* **:** Ionic compounds possess high melting and boiling points. This is because ions are tightly held together by strong electrostatic forces of attraction and hence a huge amount of energy is required to break the crystal lattice. For example order of melting and boiling points in halides of sodium and oxides of IInd group elements is as,

$$NaF > NaCl > NaBr > NaI, \quad MgO > CaO > BaO$$

(iii) *Hard and brittle* **:** Electrovalent compounds are har in nature. The hardness is due to strong forces of attraction between oppositely charged ion which keep them in their alloted positions. The brittleness of the crystals is due to movement of a layer of a crystal on the other layer by application of external force when like ions come infront of each other. The forces of repulsion come into play. The breaking of crystal occurs on account of these forces or repulsion.

(iv) *Electrical conductivity* **:** Electrovalent solids donot conduct electricity. This is because the ions remain intact occupying fixed positions in the crystal lattice. When ionic compounds are melted or dissolved in a polar solvent, the ions become free to move. They are attracted towards the respective electrode and act as current carriers. Thus, electrovalent compounds in the molten state or in solution conduct electricity.

(v) *Solubility* **:** Electrovalent compounds are fairly soluble in polar solvents and insoluble in non-polar solvents. The polar solvents have high values of dielectric constants. Water is one of the best polar solvents as it has a high value of **dielectric constant**. *The* ***dielectric constant*** *of a solvent is defined as its capacity to weaken the force of attraction between the electrical charges immersed in that solvent. In solvent like water, the electrostate force of attraction between the ions decreases. As a result there ions get separated and finally solvated.*

The values of dielectric constants of some of the compounds are given as :

Compound	Water	Methyl Alc	Ethyl Alc.	Acetone	Ether
Dielectric constant	81	35	27	21	4.1

$\longrightarrow$ Capacity to dissolve electrovalent compounds decreases

Lattice energy and solvation energy also explains the solubility of electrovalent compounds. ***These compounds dissolve in such a solvent of which the value of solvation energy is higher than the lattice energy of the compound***. The value of solvation energy depends on the relative size of the ions. Smaller the ion more of solvation, hence higher the solvation energy.

Note : ✹ Some ionic compounds *e.g.*, $BaSO_4, PbSO_4, AgCl, AgBr, AgI, Ag_2CrO_4$ etc. are sparingly soluble in water because in all such cases higher values of lattice energy predominates over solvation energy.

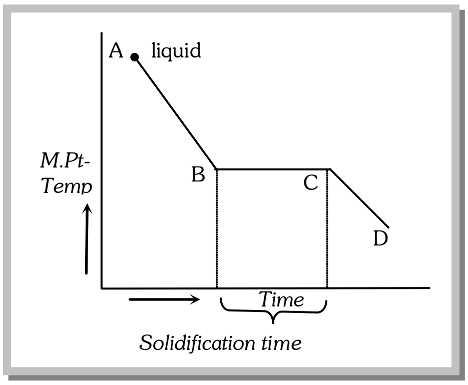
(vi) *Space isomerism* **:**The electrovalent bonds are non-rigid and non-directional. Thus these compound do not show space isomerism e.g. geometrical or optical isomerism.

(vii) *Ionic reactions* **:** Electrovalent compounds furnish ions in solution. *The chemical reaction of these compounds are ionic reactions, which are fast. Ionic bonds are more common in inorganic compounds*.

$$K^+Cl^- + \overset{+}{Ag}\,\overset{-}{NO_3} \longrightarrow \underset{\text{(Precipitate)}}{\overset{+}{Ag}\,\overset{-}{Cl}} \downarrow + \overset{+}{K}\,\overset{-}{NO_3}$$

(viii) *Isomorphism* **:** Electrovalent compounds show isomorphism. Compound having same electronic structures are isomorphous to each other.

(ix) *Cooling curve* **:** Cooling curve of an ionic compound is not smooth, it has two break points corresponding to time of solidification.



(x) *Electrovalency and Variable electrovalency* **:** *The capacity of an element to form electro-valent or ionic bond is called its electro-valency* **or** *the number of electrons lost or gained by the atom to form ionic compound is known as its electro-valency.*

Certain metallic element lose different number of electrons under different conditions, thereby showing variable electrovalency. The following are the reasons:

(a) *Unstability of core* **:** *The residue configuration left after the loss of valency electrons is called kernel or core*. In the case of the atoms of transition elements, ions formed after the loss of valency electrons do not possess a stable core as the configuration of outermost shell is not ns^2np^6 but $ns^2np^6d^{1 \text{ to } 10}$. The outer shell lose one or more electrons giving rise to metal ions of higher valencies.

Example : $Fe^{2+} \;=\; 3s^2\,3p^6\,3d^6, 4s^0$ (not stable)

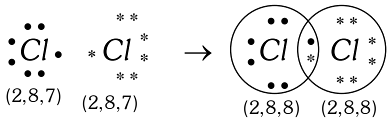
$Fe^{3+} \;=\; 3s^2\,3p^6\,3d^5, 4s^0$ (stable)

(b) *Inert pair effect* **:** Some of heavier representative elements of third, fourth and fifth groups having configuration of outermost shell $ns^2\ np^1$, $ns^2\ np^2$ and $ns^2\ np^3$ show valencies with a difference of 2, *i.e.*, (1 : 3) (2 : 4) (3 : 5) respectively. In the case of lower valencies, only the electrons present in *p*–subshell are lost and ns^2 electrons remain intact. The reluctance of *s*-electron pair to take part in bond formation is known as the inert pair effect.

Covalent bond.

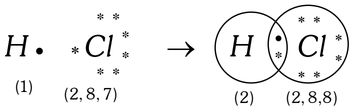
Covalent bond was first proposed by **Lewis** in 1916. *The bond formed between the two atoms by mutual sharing of electrons so as to complete their octets or duplets (in case of elements having only one shell) is called* ***covalent bond or covalent linkage.*** A covalent bond between two similar atoms is non-polar covalent bond while it is polar between two different atom having different electronegativities. Covalent bond may be single, double or a triple bond.

Example : *Formation of chlorine molecule* : chlorine atom has seven electrons in the valency shell. In the formation of chlorine molecule, each chlorine atom contributes one electron and the pair of electrons is shared between two atoms. both the atoms acquire stable configuration of argon.



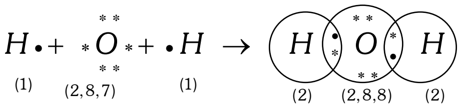
or $Cl - Cl$

Formation of HCl molecule : Both hydrogen and chlorine contribute one electron each and then the pair of electrons is equally shared. Hydrogen acquires the configuration of helium and chlorine acquires the configuration of argon.



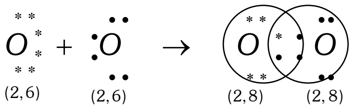
or $H-Cl$

Formation of water molecule : Oxygen atom has 6 valency electrons. It can achieve configuration of neon by sharing two electrons, one with each hydrogen atom.



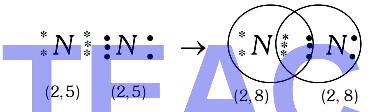
or $H-O-H$

Formation of O_2 molecule : Each oxygen atom contributes two electrons and two pairs of electrons are the shared equally. Both the atoms acquire configuration of neon.



or $O=O$

Formation of N_2 molecule : Nitrogen atom has five valency electrons. Both nitrogen atoms achieve configuration of neon by sharing 3 pairs of electrons, i.e., each atom contributes 3 electrons.



or $N \equiv N$

Some other examples are : H_2S, NH_3, HCN, PCl_3, PH_3, C_2H_2, H_2, C_2H_4, $SnCl_4$, $FeCl_3$, BH_3, graphite, $BeCl_2$ etc.

(1) Conditions for formation of covalent bonds

(i) *Number of valency electrons* **:** The combining atoms should be short by 1, 2 or 3 electrons in the valency shell in comparison to stable noble gas configuration.

(ii) *Electronegativity difference* **:** Electronegativity difference between the two atoms should be zero or very small.

(iii) *Small decrease in energy* **:** The approach of the atoms towards one another should be accompanied by decrease of energy.

(2) Characteristics of covalent compounds

(i) *Physical state* **:** These exist as gases or liquids under the normal conditions of temperature and pressure. This is because very weak forces of attraction exist between discrete molecules. Some covalent compounds exist as soft solids.

(ii) *Melting and boiling points* **:** Diamond, Carborandum (SiC), Silica (SiO_2), AlN etc. have giant three dimensional network structures; therefore have exceptionally high melting points otherwise these compounds have relatively low melting and boiling points. This is due to weak forces of attraction between the molecules.

(iii) *Electrical conductivity* **:** In general covalent substances are bad conductor of electricity. Polar covalent compounds like HCl in solution conduct electricity. Graphite can conduct electricity in solid state since electrons can pass from one layer to the other.

(iv) *Solubility* **:** These compounds are generally insoluble in polar solvent like water but soluble in non-polar solvents like benzene etc. some covalent compounds like alcohol, dissolve in water due to hydrogen bonding.

(v) *Isomerism* **:** The covalent bond is rigid and directional. These compounds, thus show isomerism (structural and space).

(vi) *Molecular reactions* : Covalent substances show molecular reactions. The reaction rates are usually low because it involves two steps (i) breaking of covalent bonds of the reactants and (ii) establishing of new bonds while the ionic reactions involved only regrouping of ions.

(vii) *Covalency and Variable covalency* **:** *The number of electrons contributed by an atom of the element for sharing with other atoms is called covalency of the element. The variable covalency of an element is equal to the total number of unpaired electrons in s, p and d-orbitals of its valency shell.*

Covalency = 8 – [Number of the group to which element belongs]

Examples : Nitrogen $_7N = \underset{2s}{\boxed{\uparrow\downarrow}}\quad \underset{2p}{\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}}$ Covalency of $N = 3$

The element such as P, S, Cl, Br, I have vacant d-orbitals in their valency shell. These elements show variable covalency by increasing the number of unpaired electrons under excited conditions. The electrons from paired orbitals get excited to vacant d-orbitals of the same shell.

Promotion energy : The energy required for excitation of electrons.

Promotion rule : Excitation of electrons in the same shell

Phosphorus : Ground state

$\underset{3s}{\boxed{\uparrow\downarrow}}\quad \underset{3p}{\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}}$ Covalency 3

Phosphorus : Excited state

$\underset{3s}{\boxed{\uparrow}}\quad \underset{3p}{\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}}\quad \underset{3d}{\boxed{\uparrow}\boxed{}\boxed{}\boxed{}\boxed{}}$ Covalency-5

PCl_3 is more stable due to inert pair effect.

Sulphur : Ground state

$\underset{3s}{\boxed{\uparrow\downarrow}}\quad \underset{3p}{\boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\uparrow}}\quad \underset{3d}{\boxed{}\boxed{}\boxed{}\boxed{}\boxed{}}$ Covalency-2 (as in SF_2)

Sulphur : Excited state

1st excited state $\underset{3s}{\boxed{\uparrow\downarrow}}\quad \underset{3p}{\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}}\quad \underset{3d}{\boxed{\uparrow}\boxed{}\boxed{}\boxed{}\boxed{}}$ Covalency-4 (as in SF_4)

2nd excited state $\underset{3s}{\boxed{\uparrow}}\quad \underset{3p}{\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}}\quad \underset{3d}{\boxed{\uparrow}\boxed{\uparrow}\boxed{}\boxed{}\boxed{}}$ Covalency-6 (as in SF_6)

So variable valency of S is 2, 4 and 6.

Iodine can have maximum 7 unpaired electrons in its orbitals. It's variable valencies are 1, 3, 5 and 7.

Four elements, H, N, O and F do not possess d-orbitals in their valency shell. Thus, such an excitation is not possible and variable valency is not shown by these elements. This is reason that NCl_3 *exists while* NCl_5 *does not.*

(3) **The Lewis theory :** The Lewis theory gave the first explanation of a covalent bond in terms of electrons that was generally accepted. **The tendency of atoms to achieve eight electrons in their outermost shell is known as lewis octet rule**. Octet rule is the basis of electronic theory of valency. It is suggested that valency electrons themselves are responsible for chemical combination. The valency electrons in atoms are shown in terms of Lewis dot formulae. To write Lewis formulae for an element, we write down its symbol surrounded by a

number of dots or crosses equal to the number of valency electrons. Lewis dot formulae are also used to represent atoms covalently bonded in a molecule. Paired and unpaired valency electrons are also indicated.

Lewis symbols for the representative elements are given in the following table :

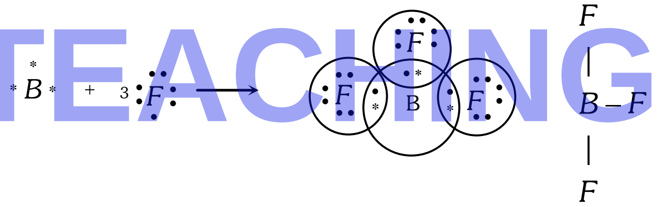
	1	2	13	14	15	16	17
Group	IA	IIA	IIIA	IVA	VA	VIA	VIIA
Lewis symbol	$X\bullet$	$\bullet X\bullet$	$\bullet\overset{\bullet}{X}\bullet$	$\bullet\overset{\bullet}{\underset{\bullet}{X}}\bullet$	$\bullet\overset{\bullet}{\underset{\bullet\bullet}{X}}\bullet$	$\bullet\overset{\bullet\bullet}{\underset{\bullet\bullet}{X}}\bullet$	$:\overset{\bullet\bullet}{\underset{\bullet\bullet}{X}}\bullet$

CO is not an exception to octet rule $:\overset{-}{C}\equiv\overset{+}{O}:$ *or* $:C\overset{\leftarrow}{\equiv}\underset{\cdot\cdot}{O}:$

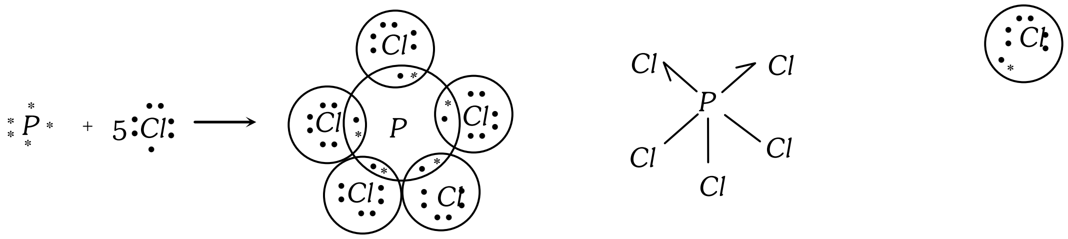
(4) **Failure of octet rule :**

There are several stable molecules known in which the octet rule is violated *i.e.*, atoms in these molecules have number of electrons in the valency shell either short of octet or more than octet.

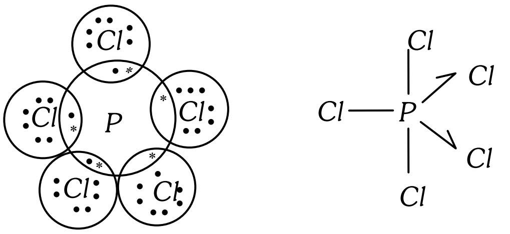
In BF_3 molecules, boron atom forms three single covalent bonds with three fluorine atoms, i.e., it attains six electrons in the outer shell.



PCl_5 molecule : Phosphorus atom have five electrons in valency shell. It forms five single covalent bonds with five chlorine atoms utilising all the valency electrons and thereby attains 10 electrons in the outer shell.



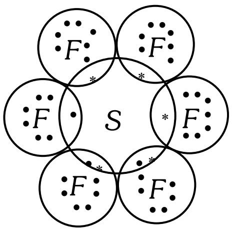
(i) *Sugden's concept of singlet linkage* explains the stability of such molecules. In PCl_5, three chlorine atoms are linked by normal covalent bonds and two chlorine atoms are linked by singlet linkages, thus, phosphorus achieves 8 electrons in the outermost shell.

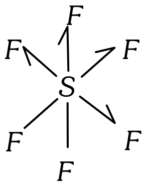


This structure indicates that the nature of two chlorine atoms is different than the other three as singlet linkage is weaker than normal covalent bond. The above observation is confirmed by the fact that on heating, PCl_5 dissociates into PCl_3 and Cl_2.

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

Similarly, in SF_6 four singlet linkages are present while in IF_7, six singlet linkages are present.





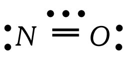
(ii) *Sidgwick's concept of maximum covalency*

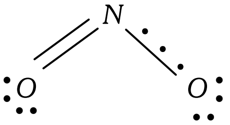
- This rule states that the covalency of an element may exceed four and octet can be exceeded.
- The maximum covalency of an element actually depends on the period of periodic table to which it belongs.
- This rule explains the formation of PCl_5 and SF_6.
- This also explains why nitrogen does not form NF_5 or NCl_5 because nitrogen belongs to second period and the maximum covalency of nitrogen is three.

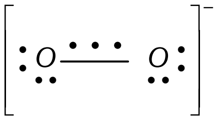
(iii) *Odd electron bond* : In 1916 Luder postulated that there are number of stable molecules in which double bonds are formed by sharing of an odd number of electrons, i.e., one, three, five, etc., between the two bonded atoms. the bonds of this type are called odd electron bonds.

The normal valence bond structure of oxygen molecule, $:\ddot{O}=\overset{**}{O}\,\substack{*\\*}$, fails to account for the paramagnetic nature of oxygen. Thus, structure involving three electrons bond has been suggested by Pauling. The following structure : $:O\underset{\cdot\ \ \cdot\ \ \cdot}{\xrightarrow{\cdot\ \ \cdot\ \ \cdot}}O:$. Explains the paramagnetic nature and high dissociation energy of oxygen molecule.

Some other examples are :


Nitric oxide (*NO*)


Nitrogen dioxide (NO_2)


Superoxide ion (O_2^-)

The number of singlet bonds = Total number of bonds – Number of electrons required to complete the octet.

Properties of Odd Electron bond

(i) The odd electron bonds are generally established either between two like atoms or between different atoms which have not more than 0.5 difference in their electronegativities.

(ii) Odd electron bonds are approximately half as strong as a normal covalent bond.

(iii) Molecules containing odd electrons are extremely reactive and have the tendency to dimerise.

(iv) Bond length of one electron bond is greater than that of a normal covalent bond. Whereas the bond length of a three electron bond is intermediate between those of a double and a triple bond.

(v) One electron bond is a resonance hybrid of the two structures i.e., $A \bullet B \longleftrightarrow A \bullet B$

Similarly, a three electron bond is a resonance hybrid of the two structures i.e., $A \bullet : B \longleftrightarrow A : \bullet B$

(5) **Construction of structures for molecules and poly atomic ions :** The following method is applicable to species in which the octet rule is not violated.

(i) Determine the total number of valence electrons in all the atoms present, including the net charge on the species (n_1).

(ii) Determine n_2 = [2 × (number of H atoms) + 8 × (number of other atoms)].

(iii) Determine the number of bonding electrons, n_3, which equals $n_2 - n_1$. No. of bonds equals $n_3/2$.

(iv) Determine the number of non-bonding electrons, n_4, which equals $n_1 - n_3$. No. of lone pairs equals $n_4/2$.

(v) Knowing the central atom (you'll need to know some chemistry here, math will not help!), arrange and distribute other atoms and $n_3/2$ bonds. Then complete octets using $n_4/2$ lone pairs.

(vi) Determine the 'formal charge' on each atom.

(vii) Formal Charge = [valence electrons in atom) – (no. of bonds) – (no. of unshared electrons)]

(viii) Other aspects like resonance etc. can now be incorporated.

Illustrative examples :

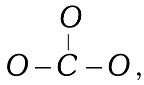
(i) $CO_3^{2-}; n_1 = 4 + (6 \times 3) + 2 = 24$ [2 added for net charge]

$n_2 = (2 \times 0) + (8 \times 4) = 32$ (no. H atom, 4 other atoms (1'C' and 3 'O')

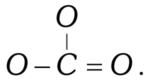
$n_3 = 32 - 24 = 8$, hence 8/2 = 4 bonds

$n_4 = 24 - 8 = 16$, hence 8 lone pairs.

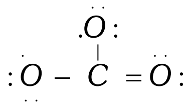
Since carbon is the central atom, 3 oxygen atoms are to be arranged around it, thus,



$O-\overset{\overset{O}{|}}{C}-O$, but total bonds are equal to 4.



Hence, we get $O-\overset{\overset{O}{|}}{C}=O$. Now, arrange lone pairs to complete octet



$:\underset{\cdot\cdot}{\overset{\cdot}{O}} - \overset{\overset{\cdot\ddot{O}:}{|}}{C} = \ddot{O}:$

(ii) CO_2; $n_1 = 4 + (6 \times 2) = 16$

$n_2 = (2 \times 0) + (8 \times 3) = 24$

$n_3 = 24 - 16 = 8$, hence 4 bonds

$n_4 = 16 - 8 = 8$, hence 4 lone-pairs

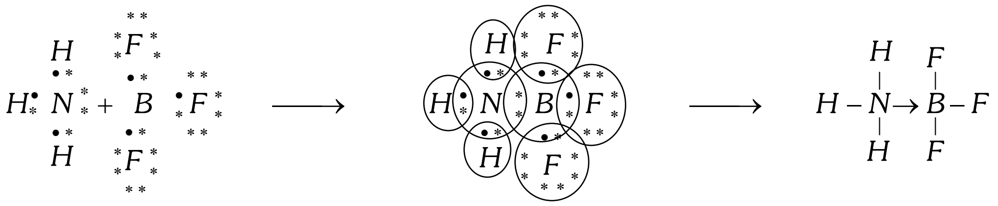
Since C is the central atom, the two oxygen atoms are around to be arranged it thus the structure would be; $O-C-O$, but total no. of bonds = 4

Thus, $O = C = O$. After arrangement of lone pairs to complete octets, we get, $:\ddot{O}=C=\ddot{O}:$ and thus final structure is $:\ddot{O}=C=\ddot{O}:$

Co-ordinate covalent or Dative bond.

This is a special type of covalent bond where the shared pair of electrons are contributed by one species only but shared by both. The atom which contributes the electrons is called the **donor** while the other which only shares the electron pair is known as **acceptor**. This bond is usually represented by an arrow (→) pointing from donor to the acceptor atom.

For example, in BF_3 molecule, boron is short of two electrons. So to complete its octet, it shares the lone pair of nitrogen in ammonia forming a dative bond as shown in figure



Formation of a co-ordinate bond between NH_3 and BF_3

Examples : CO, N_2O, H_2O_2, N_2O_3, N_2O_4, N_2O_5, HNO_3, NO_3^-, SO_2, SO_3, H_2SO_4, SO_4^{2-}, SO_2^{2-}, H_3PO_4, $H_4P_2O_7$, H_3PO_3, Al_2Cl_6 (Anhydrous), O_3, SO_2Cl_2, $SOCl_2$, HIO_3, $HClO_4$, $HClO_3$, CH_3NC, $N_2H_5^+$, CH_3NO_2, NH_4^+, $[Cu(NH_3)_4]^{2+}$ etc.

(1) Characteristics of co-ordinate covalent bond

(i) *Melting and boiling points* **:** Their melting and boiling points are higher than purely covalent compounds and lower than purely ionic compounds.

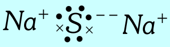
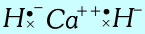
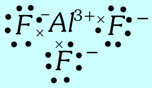
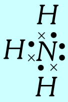
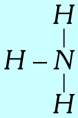
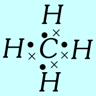
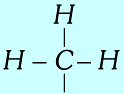
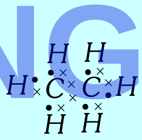
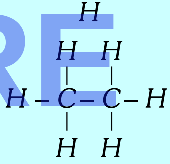
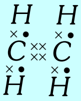
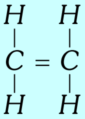
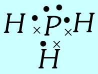
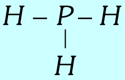
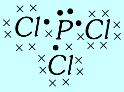
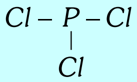
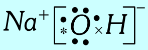
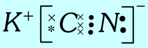
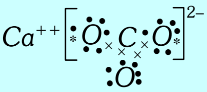
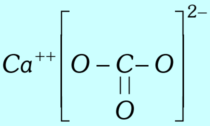
(ii) *Solubility* **:** These are sparingly soluble in polar solvent like water but readily soluble in non-polar solvents.

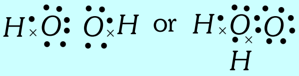
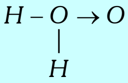
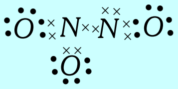
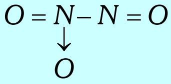
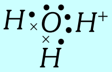
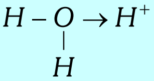
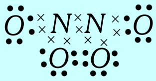
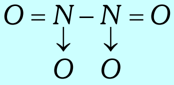
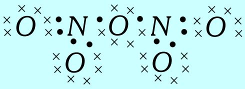
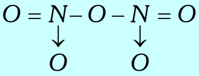
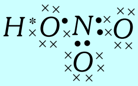
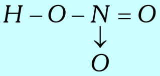
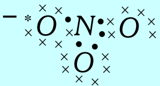
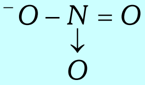
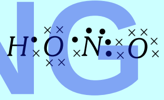
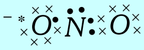
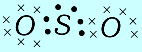
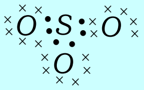
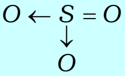
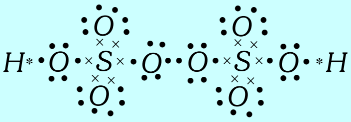
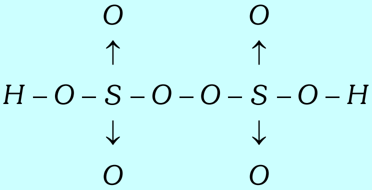
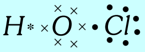
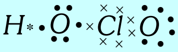
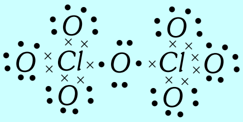
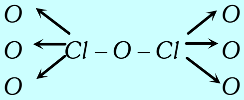
(iii) *Conductivity* **:** Like covalent compounds, these are also bad conductors of electricity. Their solutions or fused masses do not allow the passage to electricity.

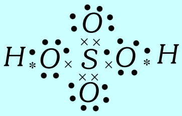
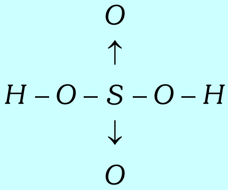
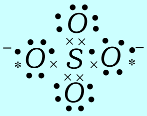
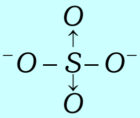
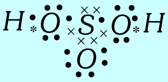
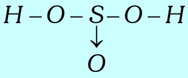
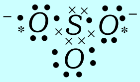
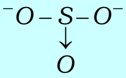
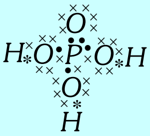
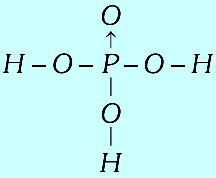
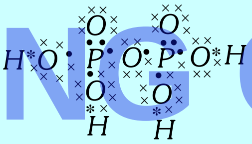
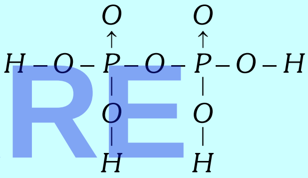
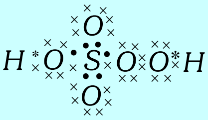
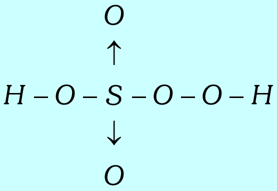
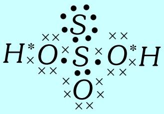
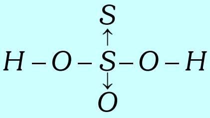
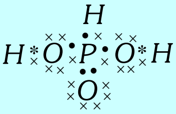
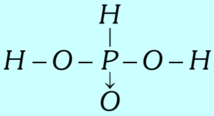
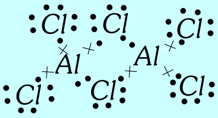
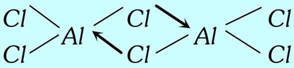
(iv) *Directional character of bond* **:** The bond is rigid and directional. Thus, coordinate compounds show isomerism.

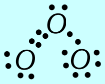
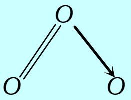
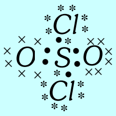
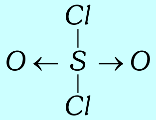
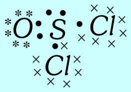
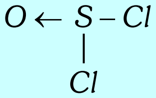
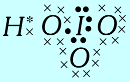
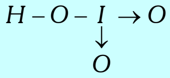
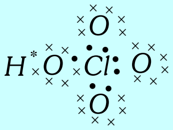
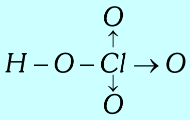
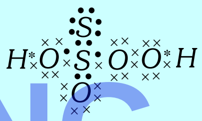
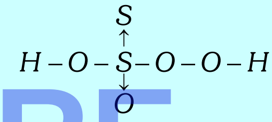
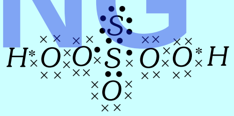
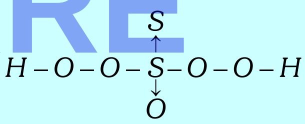
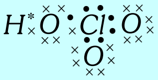
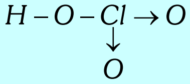
Table: Electron dot formulae and Bond formulae or Dash formulae of some compounds

No.	Molecular formula		Electron dot formula	Dash formula or Bond formula
1.	**Sodium chloride**	**NaCl**	$Na^+\ {}^{\bullet}_{\times}\overset{\bullet\bullet}{\underset{\bullet\bullet}{Cl}}\colon^{-}$	Na^+Cl^-
2.	**Magnesium chloride**	**$MgCl_2$**	${}^{\bullet}_{\times}\overset{\bullet\bullet}{\underset{\bullet\bullet}{Cl}}\colon^{-}Mg^{++}\,{}^{\bullet}_{\times}\overset{\bullet\bullet}{\underset{\bullet\bullet}{Cl}}\colon^{-}$	$Cl^-Mg^{++}Cl^-$
3.	**Calcium chloride**	**$CaCl_2$**	${}^{\bullet}_{\times}\overset{\bullet\bullet}{\underset{\bullet\bullet}{Cl}}\colon^{-}Ca^{++}\,{}^{\bullet}_{\times}\overset{\bullet\bullet}{\underset{\bullet\bullet}{Cl}}\colon^{-}$	$Cl^-Ca^{++}Cl^-$
4.	**Magnesium oxide**	**MgO**	$Mg^{++}\ {}^{\times}_{\times}\overset{\bullet\bullet}{\underset{\bullet\bullet}{O}}\colon^{--}$	$Mg^{++}O^{--}$

5.	**Sodium sulphide**	Na_2S		$Na^+S^{--}Na^+$
6.	**Calcium hydride**	CaH_2		$H^-Ca^{++}H^-$
7.	**Aluminium flouride**	AlF_3		$F^-\ Al^{3+}\ F^-$ F^-
8.	**Hydrogen chloride**	HCl		$H-Cl$
9.	**Water**	H_2O		$H-O-H$
10.	**Hydrogen sulphide**	H_2S		$H-S-H$
11.	**Ammonia**	NH_3		 $H-\underset{H}{\overset{H}{N}}$
12.	**Hydrogen cyanide**	HCN		$H-C\equiv N$
13.	**Methane**	CH_4		 $H-\underset{H}{\overset{H}{C}}-H$
14.	**Ethane**	C_2H_6		 $H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-H$
15.	**Ethene**	C_2H_4		 $\underset{H}{\overset{H}{C}}=\underset{H}{\overset{H}{C}}$
16.	**Ethyne**	C_2H_2		$H-C\equiv C-H$
17.	**Phosphene**	PH_3		 $H-\underset{H}{P}-H$
18.	**Phosphorous trichloride**	PCl_3		 $Cl-\underset{Cl}{P}-Cl$
19.	**Sodium hydroxide**	$NaOH$		$Na^+[O-H]^-$
20.	**Potassium cyanide**	KCN		$K^+[C\equiv N]^-$
21.	**Calcium carbonate**	$CaCO_3$		 $Ca^{++}\left[O-\underset{\underset{O}{\|}}{C}-O\right]^{2-}$
22.	**Carbon mono oxide**	CO		$C\equiv O$

23.	**Nitrous oxide**	N_2O		$N \equiv N \rightarrow O$
24.	**Hydrogen peroxide**	H_2O_2		$H-O-O-H$ **or**  $H-\underset{\substack{\vert\\ H}}{O}\rightarrow O$
25.	**Dinitrogen trioxide**	N_2O_3		 $O=\underset{\substack{\downarrow\\ O}}{N}-N=O$
26.	**Hydronium ion**	H_3O^+		 $H-\underset{\substack{\vert\\ H}}{O}\rightarrow H^+$
27.	**Nitrogen dioxide**	N_2O_4		 $O=\underset{\substack{\downarrow\\ O}}{N}-\underset{\substack{\downarrow\\ O}}{N}=O$
28.	**Nitrogen pentaoxide**	N_2O_5		 $O=\underset{\substack{\downarrow\\ O}}{N}-O-\underset{\substack{\downarrow\\ O}}{N}=O$
29.	**Nitric acid**	HNO_3		 $H-O-\underset{\substack{\downarrow\\ O}}{N}=O$
30.	**Nitrate ion**	NO_3^-		 $^-O-\underset{\substack{\downarrow\\ O}}{N}=O$
31.	**Nitrous acid**	HNO_2		$H-O-N=O$
32.	**Nitrite ion**	NO_2^-		$^-O-N=O$
33.	**Sulphur dioxide**	SO_2		$O\leftarrow S=O$
34.	**Sulphur trioxide**	SO_3		 $O\leftarrow\underset{\substack{\downarrow\\ O}}{S}=O$
35.	**Peroxysulphuric acid** **(Marshal acid)**	$H_2S_2O_8$		 $H-O-\overset{\substack{O\\ \uparrow}}{\underset{\substack{\downarrow\\ O}}{S}}-O-O-\overset{\substack{O\\ \uparrow}}{\underset{\substack{\downarrow\\ O}}{S}}-O-H$
36.	**Hypochlorous acid**	$HOCl$		$H-O-Cl$
37.	**Chlorous acid**	$HClO_2$		$H-O-Cl\rightarrow O$
38.	**Perchloric anhydride**	Cl_2O_7		

39.	**Sulphuric acid**	H_2SO_4		 $H-O-\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}}-O-H$
40.	**Sulphate ion**	SO_4^{2-}		 $^{-}O-\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}}-O^{-}$
41.	**Sulphurus acid**	H_2SO_3		 $H-O-\underset{\underset{O}{\downarrow}}{S}-O-H$
42.	**Sulphite ion**	SO_3^{2-}		 $^{-}O-\underset{\underset{O}{\downarrow}}{S}-O^{-}$
43.	**Phosphoric acid**	H_3PO_4		 $H-O-\overset{\overset{O}{\uparrow}}{\underset{\underset{\underset{H}{\mid}}{O}}{\mid}}{P}}-O-H$
44.	**Pyrophosphoric acid**	$H_4P_2O_7$		
45.	**Persulphuric acid (caro's acid)**	H_2SO_5		 $H-O-\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}}-O-O-H$
46.	**Thiosulphurous acid**	$H_2S_2O_3$		 $H-O-\overset{\overset{S}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}}-O-H$
47.	**Phosphorous acid**	H_3PO_3		 $H-O-\overset{\overset{H}{\mid}}{\underset{\underset{O}{\downarrow}}{P}}-O-H$
48.	**Aluminium chloride**	Al_2Cl_6 **(Anhydrous)**		

49.	**Ozone**	O_3		
50.	**Sulphuryl chloride**	SO_2Cl_2		 $O\leftarrow\overset{\overset{Cl}{\mid}}{\underset{\underset{Cl}{\mid}}{S}}\rightarrow O$
51.	**Sulphonyl chloride**	$SOCl_2$		 $O\leftarrow\underset{\underset{Cl}{\mid}}{S}-Cl$
52.	**Iodic acid**	HIO_3		 $H-O-\underset{\underset{O}{\downarrow}}{I}\rightarrow O$
53.	**Perchloric acid**	$HClO_4$		 $H-O-\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{Cl}}\rightarrow O$
54.	**Hyposulphurous acid**	$H_2S_2O_4$		 $H-O-\overset{\overset{S}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}}-O-O-H$
55.	**Pyrosulphurus acid**	$H_2S_2O_5$		 $H-O-O-\overset{\overset{S}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}}-O-O-H$
56.	**Chloric acid**	$HClO_3$		 $H-O-\underset{\underset{O}{\downarrow}}{Cl}\rightarrow O$

Polarity of covalent bond.

A covalent bond in which electrons are shared equally between bonded atoms, is called non polar covalent bond while a covalent bond, in which electrons are shared unequally and the bonded atoms acquire a partial positive and negative charge, is called a polar covalent bond. The atom having higher electronegativity draws the bonded electron pair more towards itself resulting in partial charge separation. This is the reason that HCl molecule in vapour state contains polar covalent bond

Polar covalent bond is indicated by notation : $\overset{+\delta}{H}-\overset{-\delta}{Cl}$

(1) Bond polarity in terms of ionic character : The polar covalent bond, has partial ionic character. Which usually increases with increasing difference in the electronegativity (EN) between bonded atom

	$H-F$	$H-Cl$	$H-Br$	$H-I$
EN	2.1 4.0	2.1 3.0	2.1 2.8	2.1 2.5
Difference in EN	1.9	0.9	0.7	0.4

$\longrightarrow$

Ionic character decreases as the difference in electronegativity decreases

(2) Percentage ionic character : Hennay and Smith gave the following equation for calculating the percentage of ionic character in A–B bond on the basis of the values of electronegativity of the atoms A and B.

$$\textit{Percentage of ionic character} = [16\,(\chi_A - \chi_B) + 3.5\,(\chi_A - \chi_B)^2].$$

Whereas $(x_A - x_B)$ is the electronegativity difference. This equation gives approximate calculation of percentage of ionic character, e.g., 50% ionic character corresponds to $(x_A \sim x_B)$ equals to 1.7.

Dipole moment.

"The product of magnitude of negative or positive charge (q) and the distance (d) between the centres of positive and negative charges is called dipole moment".

It is usually denoted by μ. Mathematically, it can be expressed as follows :

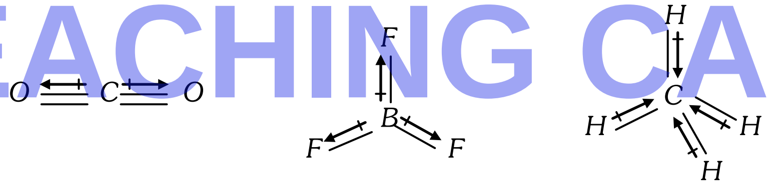
$$\mu = \text{Electric charge} \times \text{bond length}$$

As q is in the order of 10^{-10} *esu* and d is in the order of 10^{-8} *cm*, μ is in the order of 10^{-18} *esu cm*. Dipole moment is measured in "*Debye*" (D) unit. $1D = 10^{-18}$ *esu cm* = 3.33×10^{-30} *coulomb metre.*

Generally, as electronegativity difference increases in diatomic molecules, the value of dipole moment increases. Greater the value of dipole moment of a molecule, greater the polarity of the bond between the atoms.

Dipole moment is indicated by an arrow having a symbol ($\leftarrow\!\!\!+\!\!\!\rightarrow$) pointing towards the negative end. Dipole moment has both magnitude and direction and therefore it is a vector quantity.

Symmetrical polyatomic molecules *are not polar so they do not have any value of dipole moment.*



μ = 0 due to symmetry

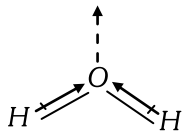
Some other examples are – CCl_4, CS_2 , $PbCl_4, SF_6, SO_3, C_6H_6$, *naphthalene and all homonuclear molecules* (H_2, O_2, Cl_2 *etc*)

Note : ☐ Benzene, Naphthalene have zero dipole moment due to planar structure.

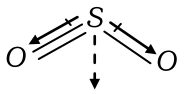
✸ Amongst isomeric dihalobenzenes, the dipole moment decreases in the order : o > m > p.

✸A molecule of the type MX_4, MX_3 has zero dipole moment, because the σ-bonding orbitals used by $M(Z < 21)$ must be sp^3, sp^2 hybridization respectively (e.g. $\underbrace{CH_4,\ CCl_4,\ SiF_4,\ SnCl_4}_{sp^3}$, $\underbrace{BF_3,\ AlCl_3}_{sp^2}$ etc.)

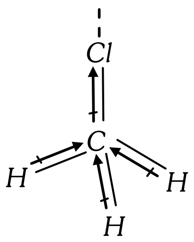
Unsymmetrical polyatomic molecules *always have net value of dipole moment, thus such molecules are polar in nature.* H_2O, CH_3Cl, NH_3, *etc are polar molecules as they have some positive values of dipole moments.*



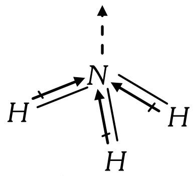
Water μ = 1.84D



Sulphur dioxide
μ = 1.60D



Methyl chloride
μ = 1.86D



Ammonia
μ = 1.46D

$\mu \neq 0$ due to unsymmetry

Some other examples are – CH_3Cl, CH_2Cl_2, $CHCl_3$, $SnCl_2$, ICl, $C_6H_5CH_3$, H_2O_2, O_3, Freon etc.

Applications of dipole moment

(i) *In determining the symmetry (or shape) of the molecules* **:** Dipole moment is an important factor in determining the shape of molecules containing three or more atoms. For instance, if any molecule possesses two or more polar bonds, it will not be symmetrical if it possesses some molecular dipole moment as in case of water $(\mu = 1.84D)$ and ammonia $(\mu = 1.49D)$. But if a molecule contains a number of similar atoms linked to the central atom and the overall dipole moment of the molecule is found to be zero, this will imply that the molecule is symmetrical, e.g., in case of BF_3, CH_4, CCl_4 etc.,

(ii) *In determining percentage ionic character* **:** Every ionic compound having some percentage of covalent character according to Fajan's rule. The percentage of ionic character in a compound having some covalent character can be calculated by the following equation.

$$\text{The percent ionic character} = \frac{\text{Observed dipole moment}}{\text{Calculated dipole moment assuming 100\% ionic bond}} \times 100$$

(iii) *In determining the polarity of bonds as bond moment* **:** As $\mu = q \times d$, obviously, *greater is the magnitude of dipole moment, higher will be the polarity of the bond*. The contribution of individual bond in the dipole moment of a polyatomic molecule is termed as bond moment. The measured dipole moment of water molecule is 1.84 D. This dipole moment is the vectorial sum of the individual bond moments of two O-H bonds having bond angle 104.5°.

Thus, $\mu_{obs} = 2\mu_{O-H}\cos 52.25$ or $1.84 = 2\mu_{O-H} \times 0.6129$; $\mu_{O-H} = 1.50\,D$

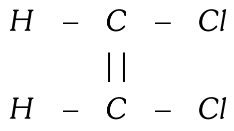
Note : ✹ $\Delta EN \propto$ dipole moment, so $HF > HCl > HBr > HI$,

✹ $\Delta EN \propto$ bond polarity, so $HF > H_2O > NH_3 > H_2S$.

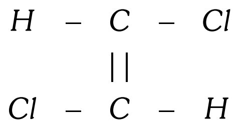
Where, ΔEN = Electronegativity difference

✹If the electronegativity of surrounding atom decreases, then dipole moment increases. $NCl_3 < NBr_3 < NI_3$

(iv) *To distinguish cis and trans forms* : The trans isomer usually possesses either zero dipole moment or very low value in comparision to *cis*–form



$$\begin{array}{ccccc} H & - & C & - & Cl \\ & & \| & & \\ H & - & C & - & Cl \end{array}$$



$$\begin{array}{ccccc} H & - & C & - & Cl \\ & & \| & & \\ Cl & - & C & - & H \end{array}$$

Cis – 1, 2 – dichloro ethene $\mu = 1.9\,D$ Trans – 1, 2 –dichloro ethene, $\mu = 0$

Example: Calculate the % of ionic character of *a* bond having length = 0.92 Å and 1.91 D as its observed dipole moment.

(a) 43.25 (b) 86.5 (c) 8.65 (d) 43.5

Solution: (a) Calculated μ considering 100% ionic bond [When we consider a compound ionic, then each ionic sphere should have one electron charge on it of $4.80 \times 10^{-10}\,esu$ (in CGS unit) or $1.60 \times 10^{-19}\,C$ (in SI unit)]

$= 4.8 \times 10^{-10} \times 0.92 \times 10^{-8}\,esu\ cm = 4.416\,D$

$$\%\ \text{Ionic character} = \frac{1.91}{4.416} \times 100 = 43.25.$$

Important Tips

- *The dipole moment of CO molecule is greater than expected. This is due to the presence of a dative (co-ordinate) bond.*
- *Critical temperature of water is higher than that of O_2 because H_2O molecule has dipole moment.*
- *Liquid is not deflected by a non uniform electrostatic field in hexane because of $\mu = 0$*

Change of ionic character to covalent character and Fajan's rule.

Although in an ionic compound like M^+X^- the bond is considered to be 100% ionic, but it has some covalent character. The partial covalent character of an ionic bond has been explained on the basis of polarization.

Polarization **:** When a cation of small size approaches an anion, the electron cloud of the bigger anion is attracted towards the cation and hence gets distorted. This distortion effect is called polarization of the anion. The power of the cation to polarize nearby anion is called its polarizing power. The tendency of an anion to get distorted or polarized by the cation is called polarizability. Due to polarization, some sort of sharing electrons occurs between two ions and the bond shows some covalent character.

Fajan's rule : The magnitude of polarization or increased covalent character depends upon a number of factors. These factors were suggested by Fajan and are known as Fajan's rules.

Factors favouring the covalent character

(i) *Small size of cation : Smaller size of cation greater is its polarizing power i.e. greater will be the covalent nature of the bond*. On moving down a group, the polarizing power of the cation goes on decreasing. While it increases on moving left to right in a period. Thus polarizing power of cation follows the order $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$. This explains why $LiCl$ is more covalent than KCl.

(ii) *Large size of anion : Larger the size of anion greater is its polarizing power i.e. greater will be the covalent nature of the bond*. The polarizability of the anions by a given cation decreases in moving left to right in a period. While it increases on moving down a group. Thus polarzibility of the anion follows the order $I^- > Br^- > Cl^- > F^-$. This explains why iodides are most covalent in nature.

(iii) *Large charge on either of the two ions : As the charge on the ion increases, the electrostatic attraction of the cation for the outer electrons of the anion also increases with the result its ability for forming the covalent bond increases. $FeCl_3$ has a greater covalent character than $FeCl_2$.* This is because Fe^{3+} ion has greater charge and smaller size than Fe^{2+} ion. As a result Fe^{3+} ion has greater polarizing power. Covalent character of lithium halides is in the order $LiF < LiCl < LiBr < LiI$.

(iv) *Electronic configuration of the cation* : For the two ions of the same size and charge, one with a pseudo noble gas configuration (i.e. 18 electrons in the outermost shell) will be more polarizing than a cation with noble gas configuration (i.e., 8 electron in outer most shell). *CuCl* is more covalent than *NaCl,* because Cu^+ contains *18* electrons in outermost shell which brings greater polarization of the anion.

Important tips

- Δ_{en} *(Electronegativity difference)* $\propto \dfrac{\text{Ionic character}}{\text{Covalent character}}$
- *Increase of polarization brings more of covalent character in an ionic compound. The increased covalent character is indicated by the decrease in melting point of the ionic compound*
- *Decreasing trends of melting points with increased covalent character*

  $NaF < NaCl < NaBr < NaI$ *(size of anion increases)*
  M.Pt (°C) 988 801 755 651

  $BaCl_2 < SrCl_2 < CaCl_2 < MgCl_2 < BeCl_2$ *(size of cation decreases)*
  M.Pt (°C) 960 872 772 712 405
- *Lithium salts are soluble in organic solvents because of their covalent character*
- *Sulphides are less soluble in water than oxides of the same metal due to the covalent nature of sulphur.*

Quantum theory (Modern theory) of covalent bond and overlapping.

(1) A modern Approach for covalent bond (Valence bond theory or VBT)

(i) *Heitler and London concept.*

(a) To form a covalent bond, two atoms must come close to each other so that orbitals of one overlaps with the other.

(b) Orbitals having unpaired electrons of anti spin overlaps with each other.

(c) After overlapping a new localized bond orbital is formed which has maximum probability of finding electrons.

(d) Covalent bond is formed due to electrostatic attraction between radii and the accumulated electrons cloud and by attraction between spins of anti spin electrons.

(e) *Greater is the overlapping, lesser will be the bond length, more will be attraction and more will be bond energy and the stability of bond will also be high*.

(ii) *Pauling and slater extension*

(a) The extent of overlapping depends upon: Nature of orbitals involved in overlapping, and nature of overlapping.

(b) More closer the valence shells are to the nucleus, more will be the overlapping and the bond energy will also be high.

(c) Between two sub shells of same energy level, the sub shell more directionally concentrated shows more overlapping. Bond energy : $2s-2s < 2s-2p < 2p-2p$

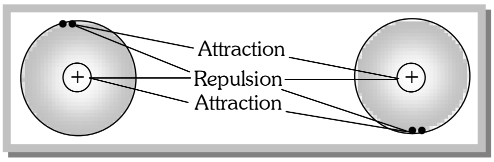
(d) s-orbitals are spherically symmetrical and thus show only head on overlapping. On the other hand, p-orbitals are directionally concentrated and thus show either head on overlapping or lateral overlapping.

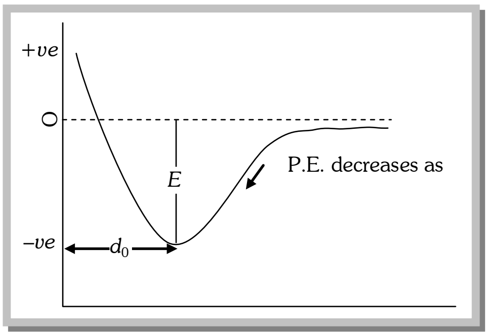
(iii) *Energy concept*

(a) Atoms combine with each other to minimize their energy.

(b) Let us take the example of hydrogen molecule in which the bond between two hydrogen atoms is quite strong.

(c) During the formation of hydrogen molecule, when two hydrogen atoms approach each other, two types of interaction become operative as shown in figure. The force of attraction between the molecules of one atom and electrons of the other atom. The force of repulsion between the nuclei of reacting atoms and electrons of the reacting atoms





(d) As the two hydrogen atoms approach each other from the infinite distance, they start interacting with each other *when the magnitude of attractive forces is more than that of repulsive forces a bond is developed between two atoms*.

(e) The decrease in potential energy taking place during formation of hydrogen molecule may be shown graphically (→)

(f) The inter nuclear distance at the point O have minimum energy or maximum stability is called bond length.

(g) *The amount of energy released (i.e., decrease in potential energy) is known as enthalpy of formation.*

(h) From the curve it is apparent that *greater the decrease in potential energy, stronger will be the bond formed* and vice versa.

(i) It is to be noted that for dissociation of hydrogen molecule into atoms, equivalent amount of energy is to be supplied.

(j) Obviously in general, a *stronger bond will require greater amount of energy for the separation of atoms. The energy required to cleave one mole of bonds of the same kind is known as the bond energy or bond dissociation energy*. This is also called as orbital overlap concept of covalent bond.

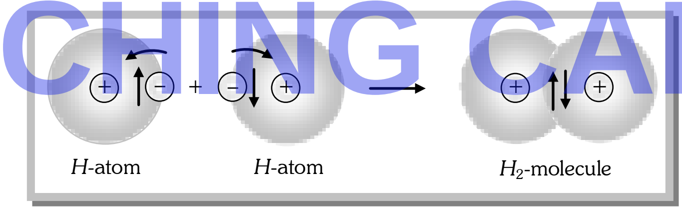
(2) Overlapping

(i) According to this concept *a covalent bond is formed by the partial overlapping of two half filled atomic orbitals containing one electron each with opposite spins then they merge to form a new orbital known as* **molecular orbital**.

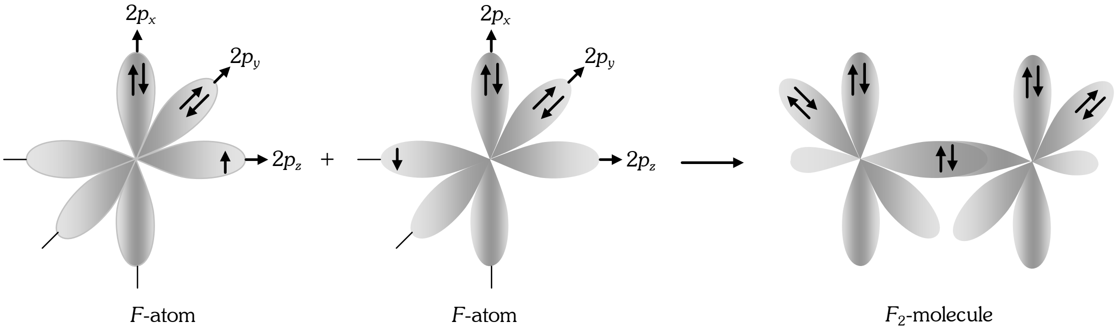
(ii) These two electrons have greater probability of their presence in the region of overlap and thus get stabilised *i.e., during overlapping energy is released.*

Examples of overlapping are given below :

Formation of hydrogen molecule **:** Two hydrogen atoms having electrons with opposite spins come close to each other, their *s*-orbitals overlap with each other resulting in the union of two atoms to form a molecule.



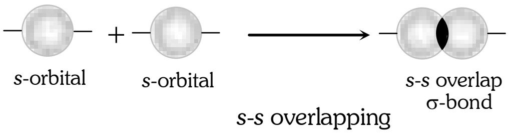
Formation of fluorine molecule **:** In the formation of F_2 molecule *p*-orbitals of each flourine atom having electrons with opposite spins come close to each other, overlapping take place resulting is the union of two atoms.



Formation of fluorine molecule

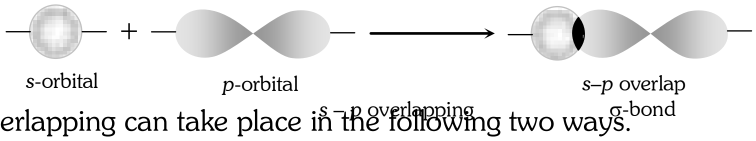
Types of overlapping and nature of covalent bonds (σ - and π - bonds) **:** overlapping of different type gives sigma (σ) and pi (π) bond. Various modes of overlapping given below :

s – s overlapping : In this type two half filled s-orbitals overlap along the internuclear axis to form σ-bond.



s-s overlapping

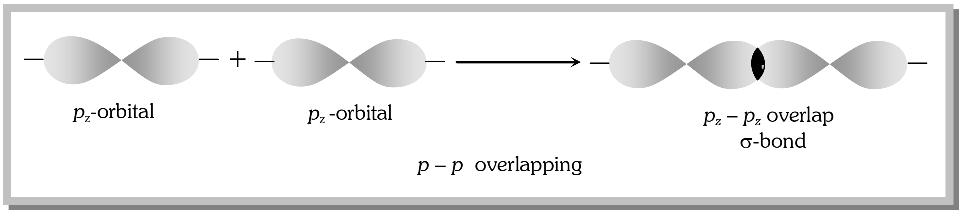
s-p overlapping : *It involves the overlapping of half filled s-orbital of one atom with the half filled p-orbital of other atom This overlapping again gives σ-bond e.g.*, formation of $H - F$ molecule involves the overlapping of 1*s* orbital of *H* with the half filled $2p_z$ – orbital of Fluorine.



s – p overlapping

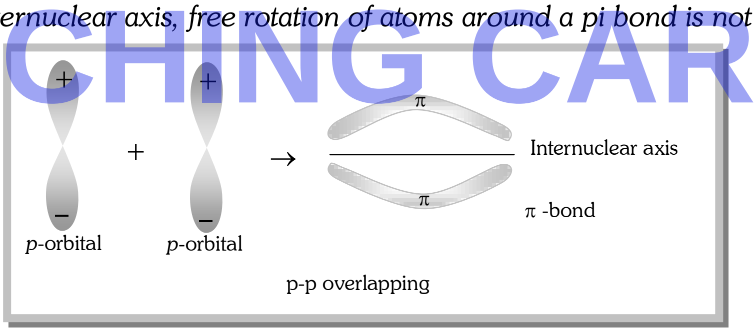
p-p overlapping : *p-p* overlapping can take place in the following two ways.

(i) *When there is the coaxial overlapping between p-orbitals of one atom with the p-orbitals of the other then σ-bond formation take place e.g.*, formation of F_2 molecule in which $2p_z$ orbital of one *F* atom overlap coaxially with the $2p_z$ orbitals of second atom. σ-bond formation take place as shown below :



$p - p$ overlapping

(ii) *When p–orbitals involved in overlapping are parallel and perpendicular to the internuclear axis. This types of overlapping results in formation of pi bond. It is always accompanied by a σ bond and consists of two charge clouds i.e., above and below the plane of sigma bond. Since overlapping takes place on both sides of the internuclear axis, free rotation of atoms around a pi bond is not possible.*



p-p overlapping

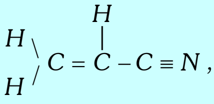
Table : Difference in σ and π bonds

Sigma (σ) bond	***Pi (π) bond***
It results from the end to end overlapping of two s-orbitals or two p-orbitals or one s and one p-orbital.	**It result from the sidewise (lateral) overlapping of two p-orbitals.**
Stronger	**Less strong**
Bond energy 80 kcals	**Bond energy 65 kcals**
More stable	**Less stable**
Less reactive	**More reactive**
Can exist independently	**Always exist along with a σ-bond**
The electron cloud is symmetrical about the internuclear axis.	**The electron cloud is above and below the plane of internuclear axis.**

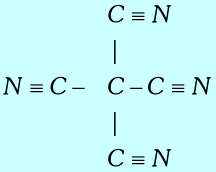
Important Tips

- *To count the σ and π bonds in molecule having single, double and triple bond first we write its expanded structure.*

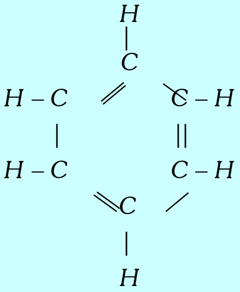
ex. $\underset{\sigma}{H-H}$, $O\overset{\sigma}{\underset{\pi}{=}}O$, $N\overset{\sigma}{\underset{2\pi}{\equiv}}N$,



$(3\pi, 6\sigma)$



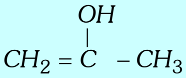
$(8\pi, 8\sigma)$



$(3\pi, 12\sigma)$

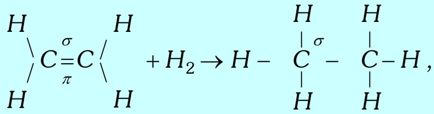
All the single bonds are σ-bond. In a double bond, one will be σ and the other π type while in a triple bond, one will be σ and other two π.

- *The enolic form of acetone has 9σ, 1π and two lone pairs*



$CH_2=\overset{OH}{\overset{|}{C}}-CH_3$ *(enol form of acetone)*

- *It is the π bond that actually takes part in reaction,*



$H_2C\overset{\sigma}{\underset{\pi}{=}}CH_2 + H_2 \rightarrow H-\overset{H}{\underset{H}{C}}\overset{\sigma}{-}\overset{H}{\underset{H}{C}}-H$

, but the shape of molecule is decided by σ-bond.

- *The number of sp^2-s sigma bonds in benzene are 6.*
- *When two atoms of the element having same spin of electron approach for bonding, the orbital overlapping and bonding both does not occur.*
- *Head on overlapping is more stronger than lateral, or sidewise overlapping.*

$$\underbrace{p\text{-}p > s\text{-}p > s\text{-}s}_{\text{Head on overlapping}} > \underbrace{p\text{-}p}_{\text{Sidewise overlapping}}$$

Hybridization.

The concept of hybridization was introduced by **Pauling** and **Slater**. It is defined as the intermixing of dissimilar orbitals of the same atom but having slightly different energies to form same number of new orbitals of equal energies and identical shapes. The new orbitals so formed are known as hybrid orbitals.

Characteristics of hybridization

(1) Only orbitals of almost similar energies and belonging to the same atom or ion undergoes hybridization.

(2) *Hybridization takes place only in orbitals, electrons are not involved in it.*

(3) The number of hybrid orbitals produced is equal to the number of pure orbitals, mixed during hybridization.

(4) In the excited state, the number of unpaired electrons must correspond to the oxidation state of the central atom in the molecule.

(5) Both half filled orbitals or fully filled orbitals of equivalent energy can involve in hybridization.

(6) *Hybrid orbitals form only sigma bonds.*

(7) *Orbitals involved in π bond formation do not participate in hybridization.*

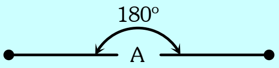
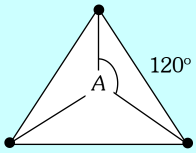
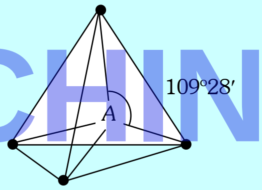
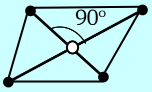
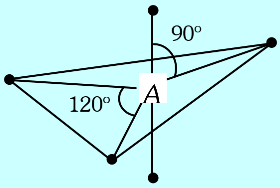
(8) *Hybridization never takes place in an isolated atom but it occurs only at the time of bond formation.*

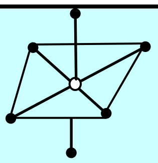
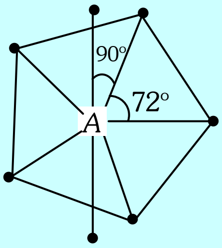
(9) *The hybrid orbitals are distributed in space as apart as possible resulting in a definite geometry of molecule.*

(10) *Hybridized orbitals provide efficient overlapping than overlapping by pure s, p and d-orbitals.*

(11) *Hybridized orbitals possess lower energy*.

Depending upon the type and number of orbitals involved in intermixing, the hybridization can be of various types namely *sp*, sp^2, sp^3, sp^3d, dsp^2, sp^3d^2, sp^3d^3. The nature and number of orbitals involved in the above mentioned types of hybridization and their acquired shapes are discussed in following table

Type of hybrisation	*Character*	*Geometry of molecules as per VSPER theory*	*No. of bonded atoms*	*No. of lone pairs*	*Actual shape of molecules*	*Example*
sp	**s-character=50%,** **p-character= 50%**	 Linear	**2**	**0**	**Linear**	$CO_2, HgCl_2, BeF_2, ZnCl_2$, $MgCl_2, C_2H_2, HCN, BeH_2$ $C_2H_2, CS_2, N_2O, Hg_2Cl_2$, $[Ag\{NH_3)_2]^+$
sp^2	**s-character= 33.33%,** **p-character=66.67%**	 Trigonal Planar, 120°	**3**	**0**	**Trigonal Planar**	$BF_3, AlCl_3, SO_3^{--}, C_2H_4$, $NO_3^-, CO_3^{2-}, HCHO$ C_6H_6, CH_3^+ **graphite,** C_2Cl_4, $C_2H_2Cl_2, [HgI_3]^-$, $[Cu(PMe_3)_3]^-$
		<120°	**2**	**1**	**V-shape (bent)**	$NO_2^-, SO_2, SnCl_2$
sp^3	**s-character = 25%,** **p-character = 75%**	 Tetrahedral , 109.5°	**4**	**0**	**Tetrahedral**	$CH_4, SiH_4, SO_4^{2-}, SnCl_4$, $ClO_4^-, BF_4^-, NH_4^+, CCl_4$, SiF_4, H_2-NH_2, $[BeF_4]^-, XeO_4$, $[AlCl_4]^-, SnCl_4, PH_4^+$, **Diamond, silica,** $Ni(CO)_4, Si(CH_3)_4, SiC$, $SF_2, [NiCl_4]^2, [MnO_4]^-[VO_4]^{3-}$
		< 109.5°	**3**	**1**	**Trigonal pyramidal**	NH_3, PCl_3, PH_3, AsH_3 $ClO_3^-, POCl_3$ H_3O^+, XeO_3
		104.5°	**2**	**2**	**V-shape (bent)**	$H_2O, H_2S, PbCl_2, OF_2, NH_2^-$ ClO_2
dsp^2	**s-character = 25%** **p – character = 50%** **d – character = 25%**	 **Square planar**	**4**	**0**	**Square planar**	$[Cu(NH_3)_4]^{2+}, [Ni(CN)_4]^{2+}$ $[Pt(NH_3)_4]^{2+}$
sp^3d	**s-character = 20%,** **p-character = 60%,** **d-character = 20%**	 **Trigonal bipyramidal**	**5**	**0**	**Trigonal bipyramidal**	$PCl_5, SbCl_5, XeO_3F_2, PF_5$ $AsF_5, PCl_4^+, PCl_6^-, [Cu(Cl)_5]^{3-}$ $[Ni(CN)_5]^{3-}$, $[Fe(CO)_5]$
			4	**1**	**Irregular tetrahedral**	$TeCl_4, SF_4$
			3	**2**	**T-shaped**	ClF_3, IF_3

			2	**3**	**Linear**	I_3^-, XeF_2
sp^3d^2	**s-character = 25%** **p – character = 50%** **d – character = 25%**	 **Octohedral**	**6**	**0**	**Octahedral**	SF_6, PF_6^-, $SnCl_6^-$, MoF_6, $(BaCl_6)^-$, $(PF_6)^-$, $[Fe(CN)_6]^{4-}$, $[Fe(H_2O)_6]^{3+}$
			5	**1**	**Square pyramidal**	ICl_5, BrF_5, IF_5 $XeOF_4$
			4	**2**	**Square planar**	XeF_4, ICl_4^-
sp^3d^3	**s-character= 14.28%,** **p-character= 42.86%,** **d-character= 42.86%**	 **Pentagonal bipyramidal**	**7**	**0**	**Pentagonal bipyramidal**	IF_7, $[ZrF_7]^{3-}$ $[UF_7]^{3-}$ $[UO_2F_5]^{3-}$
			6	**1**	**Distorted octahedral**	XeF_6

Short trick to find out hybridization **:** The structure of any molecule can be predicted on the basis of hybridization which in turn can be known by the following general formulation. $\boxed{H = \frac{1}{2}(V + M - C + A)}$

Where H = Number of orbitals involved in hybridization viz. 2, 3, 4, 5, 6 and 7, hence nature of hybridization will be sp, sp^2, sp^3, sp^3d, sp^3d^2, sp^3d^3 respectively.

V = Number electrons in valence shell of the central atom,

M = Number of monovalent atom

C = Charge on cation,

A = Charge on anion

Few examples are given below to illustrate this:

***Type* :** **(A)** When the central atom is surrounded by monovalent atoms only, e.g. BeF_2, BCl_3, CCl_4, NCl_3, PCl_5, NH_3, H_2O, OF_2, $TeCl_4$, SCl_2, IF_7, ClF_3, SF_4, SF_6, XeF_2, XeF_4, etc. Let us take the case of PCl_5. $H = \frac{1}{2}(5 + 5 - 0 + 0) = 5$. Thus, the type of hybridization is sp^3d.

***Type* :** **(B)** When the central atom is surrounded by divalent atoms only; e.g. CO_2, CS_2, SO_2, SO_3, XeO_3 etc. Let us take the case of SO_3. $H = \frac{1}{2}(6 + 0 - 0 + 0) = 3$. Thus, the type of hybridization in SO_3 is sp^2.

***Type* :** **(C)** When the central atom is surrounded by monovalent as well as divalent atoms, e.g. $COCl_2$, $POCl_3$, XeO_2F_2 etc. Let us take the case of $POCl_3$. $H = \frac{1}{2}(5 + 3 - 0 + 0) = 4$. Thus, the nature of hybridization in $POCl_3$ is sp^3.

***Type* : (D)** When the species is a cation, e.g. NH_4^+, CH_3^+, H_3O^+ etc. Let us take the case of CH_3^+. $H = \frac{1}{2}(4+3-1+0) = 3$. Thus, the hybridization in CH_3^+ is sp^2.

***Type* : (E)** When the species is an anion, e.g. SO_4^{2-}, CO_3^{2-}, PO_4^{3-}, NO_2^-, NO_3^-, etc. Let us take the case of SO_4^{2-}. $H = \frac{1}{2}(6+0-0+2) = 4$. Thus, hybridization in SO_4^{2-} is sp^3.

***Type* : (F)** When the species is a complex ion of the type ICl_4^-, I_3^-, ClF_2^-, etc. Let us take the case of ClF_2^-. $H = \frac{1}{2}(7+2-0+1) = 5$. Thus, in ClF_2^-, Cl is sp^3d hybridized.

***Type* : (G)** When the species is a complex ion of the type $[PtF_6]^{2-}$, $[Co(NH_3)_6]^{2+}$, $[Ni(NH_3)_4Cl_2]$ etc. In such cases nature of hybridization is given by counting the co-ordination number.

Important Tips

- *The sequence of relative energy and size of s – p type hybrid orbitals is* $\mathbf{sp < sp^2 < sp^3}$.
- *The relative value of the overlapping power of sp, sp^2 and sp^3 hybrid orbitals are 1.93, 1.99 and 2.00 respectively.*
- *An increase in s-character of hybrid orbitals, increases the bond angle. Increasing order of s-characters and bond angle is* $\mathbf{sp^3 < sp^2 < sp}$.
- *Normally hybrid orbitals (sp, sp^2, sp^3, dsp^2, dsp^3 etc.) form σ-bonds but in benzyne lateral overlap of sp^2-orbitals forms a π-bond.*
- *Some iso-structural pairs are $[NF_3, H_3O^+]$, $[NO_3^-, BF_3]$, $[SO_4^{2-}, BF_4^-]$. There structures are similar due to same hybridization.*
- *In BF_3 all atoms are co-planar.*

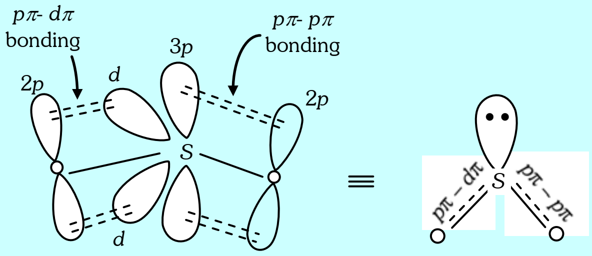
  In PCl_5 the state of hybridization of P atom is sp^3d. In its trigonal bipyramidal shape all the P-Cl bonds are not equal.

- *The π bond formed between S and O atoms in SO_2 molecule is due to overlap between their p-orbitals ($P\pi - P\pi$ bonding) or between p orbital of O-atom with d-orbital of S-atom (called $p\pi - d\pi$ bonding)*

$${}_{16}S = 1s^2 2s^2 2p^6 3s^2 3p_x^2 3p_y^1 3p_z^1 \quad \text{(Ground state configuration)}$$

$$= 1s^2 2s^2 2p^6 3s^2 3p_x^1 3p_y^1 3p_z^1 3d^1 \quad \text{(Excited state configuration)}$$

$${}_8O = 1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$$



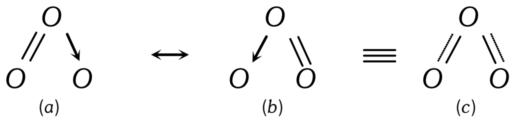
S-atom undergoes sp^2 hybridization leaving one half-filled $3p_z$ orbital and one d-orbital unhybridized. Out of two half filled orbitals of O-atom, one is involved in formation of σ-bond with S-atom and the other in forming π-bond.

Resonance.

The phenomenon of resonance was put forward by **Heisenberg** to explain the properties of certain molecules.

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

To illustrate this, consider a molecule of ozone O_3. Its structure can be written as



It may be noted that the resonating structures have no real existence. Such structures are only theoretical. In fact, the actual molecule has no pictorial representation. The resonating structures are only a convenient way of picturing molecule to account for its properties.

As a resonance hybrid of above two structures (*a*) and (*b*). For simplicity, ozone may be represented by structure (*c*), which shows the resonance hybrid having equal bonds between single and double.

Resonance is shown by benzene, toluene, O_3*, allenes* ($>C = C = C<$)*,* CO*,* CO_2*,* CO_3^-*,* SO_3*,* NO*,* NO_2 *while it is not shown by* H_2O_2*,* H_2O*,* NH_3*,* CH_4*,* SiO_2*.*

(1) Conditions for writing resonance structures

The resonance contributing structures :

(i) Should have same atomic positions.

(ii) Should have same number of bond pairs and lone pairs.

(iii) Should have nearly same energy.

(iv) Should be so written such that negative charge is present on an electronegative atom and positive charge is present on an electropositive atom.

(v) The like charges should not reside on adjacent atoms. But unlike charges should not greatly separated.

(2) Characteristics of resonance

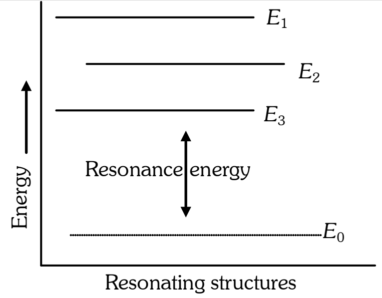
(i) The contributing structures (canonical forms) do not have any real existence. They are only imaginary. Only the resonance hybrid has the real existence.

(ii) As a result of resonance, the bond lengths of single and double bond in a molecule become equal e.g. $O–O$ bond lengths in ozone or $C–O$ bond lengths in CO_3^{2-} ion.

(iii) *The resonance hybrid has lower energy and hence greater stability than any of the contributing structures.*

(iv) *Greater is the resonance energy, greater is the stability of the molecule.*

(v) *Greater is the number of canonical forms especially with nearly same energy, greater is the stability of the molecule.*



Concept of resonance energy. Energies E_1*,* E_2 *and* E_3 *for three structures and* E_0 *is the experimentally determined bond energy*

(3) Resonance energy

It is the difference between the energy of resonance hybrid and that of the most stable of the resonating structures (having least energy). Thus,

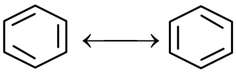
Resonance energy = Energy of resonance hybrid – Energy of the most stable of resonating structure.

(4) Bond order calculation

In the case of molecules or ions having resonance, the bond order changes and is calculated as follows:

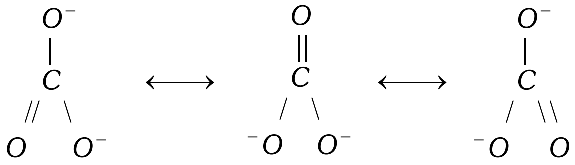
$$\text{Bond order} = \frac{\text{Total no. of bonds between two atoms in all the structures}}{\text{Total no. of resonating structures}}$$

e.g., (i) In benzene



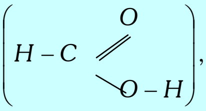
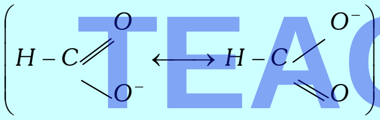
$$\text{Bond order} = \frac{\text{double bond + single bond}}{2} = \frac{2+1}{2} = 1.5$$

(ii) In carbonate ion



$$\text{Bond order} = \frac{2+1+1}{3} = 1.33$$

Important Tips

- Resonance structure (canonical form) must be planar.
- In case of formic acid  , the two $C-O$ bond lengths are different but in formate ion  the two $C-O$ bond lengths are equal due to resonance.

- In resonance hybrid, the bond lengths are different from those in the contributing structure.
- Resonance arises due to delocalisation of π electrons. Resonating structures have different electronic arrangements.
- The resonating structures do not have real existence.
- Resonance energy = [Experimental heat of formation]–[Calculated heat of formation of most stable canonical form].
- Three contributing structure of CO_2 molecule are – $O = C = O \leftrightarrow \overset{+}{O} \equiv C - \overset{-}{O} \leftrightarrow \overset{-}{O} - C \equiv \overset{+}{O}$
- Resonance structure of carbon monoxide is $:C = \underset{\cdot\cdot}{\overset{\cdot\cdot}{O}} \leftrightarrow :C \overset{\leftarrow}{=} O:$
- Resonance energy of benzene is $152.0\ kJ/mol$.

Bond characteristics.

(1) Bond length

"The average distance between the centre of the nuclei of the two bonded atoms is called bond length".

It is expressed in terms of Angstrom (1 Å = 10^{-10} *m*) or picometer (1pm = 10^{-12} *m*). It is determined experimentally by X-ray diffraction methods or spectroscopic methods. In an ionic compound, the bond length is the sum of their ionic radii ($d = r_+ + r_-$) and in a covalent compound, it is the sum of their covalent radii (*e.g.*, for HCl, $d = r_H + r_{Cl}$).

Factors affecting bond length

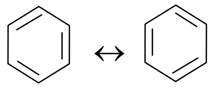
(i) *Size of the atoms* **:** *The bond length increases with increase in the size of the atoms*. For example, bond length of $H-X$ are in the order , $HI > HBr > HCl > HF$

(ii) *Electronegativity difference* **:** Bond length $\times \frac{1}{\Delta \text{EN}}$.

(iii) *Multiplicity of bond* **:** *The bond length decreases with the multiplicity of the bond. Thus, bond length of carbon–carbon bonds are in the order ,* $C \equiv C < C = C < C - C$

(iv) *Type of hybridisation* **:** As an s-orbital is smaller in size, *greater the s-character shorter is the hybrid orbital and hence shorter is the bond length. For example,* $sp^3\, C - H > sp^2\, C - H > sp\, C - H$

(v) *Resonance* **:** Bond length is also affected by resonance as in benzene and CO_2. In benzene bond length is $1.39 \mathring{A}$ which is in between $C - C$ bond length $1.54 \mathring{A}$ and $C = C$ bond length $1.34 \mathring{A}$



In CO_2 the C-O bond length is $1.15\, \mathring{A}$.

(In between $C \equiv O$ and $C = O$)

$$O = C = O \leftrightarrow \overline{O} - C \equiv \overset{+}{O} \leftrightarrow \overset{+}{O} \equiv C - \overline{O}$$

(vi) *Polarity of bond* **:** Polar bond length is usually smaller than the theoretical non-polar bond length.

(2) Bond energy

"The amount of energy required to break one mole of bonds of a particular type so as to separate them into gaseous atoms is called **bond dissociation energy** or simply **bond energy**". *Greater is the bond energy, stronger is the bond.*

Bond energy is usually expressed in $kJ\, mol^{-1}$.

Factors affecting bond energy

(i) *Size of the atoms* **:** Bond energy $\propto \frac{1}{\text{atomic size}}$ *Greater the size of the atom, greater is the bond length and less is the bond dissociation energy i.e. less is the bond strength.*

(ii) *Multiplicity of bonds* : For the bond between the two similar atoms, *greater is the multiplicity of the bond, greater is the bond dissociation energy*. This is firstly because atoms come closer and secondly, the number of bonds to be broken is more, $C - C < C = C < C \equiv C$, $C \equiv C < C \equiv N < N \equiv N$

(iii) *Number of lone pairs of electrons present* **:** *Greater the number of lone pairs of electrons present on the bonded atoms, greater is the repulsion between the atoms and hence less is the bond dissociation energy*. For example for a few single bonds, we have

Bond	***C – C***	***N – N***	***O – O***	***F – F***
Lone pair of electrons	**0**	**1**	**2**	**3**
Bond energy (kJ mol^{-1})	**348**	**163**	**146**	**139**

(iv) *Percentage s–character* : The bond energy increases as the hybrid orbitals have greater amount of s orbital contribution. Thus, *bond energy decreases in the following order*, $sp > sp^2 > sp^3$

(v) *Bond polarity* **:** *Greater the electronegativity difference, greater is the bond polarity and hence greater will be the bond strength i.e., bond energy,* $H - F > H - Cl > H - Br > H - I$,

(vi) Among halogens $Cl-Cl > F-F > Br-Br > I-I$, (Decreasing order of bond energy)

(vii) *Resonance* **:** Resonance increases bond energy.

(3) Bond angle

In case of *molecules made up of three or more atoms, the average angle between the bonded orbitals (i.e., between the two covalent bonds) is known as bond angle* θ.

Factors affecting bond angle

(i) *Repulsion between atoms or groups attached to the central atom* **:** The positive charge, developed due to high electronegativity of oxygen, on the two hydrogen atoms in water causes repulsion among themselves which increases the bond angle, *H–O–H* from 90° to 105°.

(ii) *Hybridisation of bonding orbitals* **:** In hybridisation *as the s character of the s hybrid bond increases, the bond angle increases*.

Bond type	sp^3	sp^2	sp
Bond angle	**109°28′**	**120°**	**180°**

(iii) *Repulsion due to non-bonded electrons* **:** *Bond angle* $\propto \frac{1}{\text{No. of lone pair of electrons}}$. *By increasing lone pair of electron, bond angle decreases approximately by 2.5%.*

	CH_4	NH_3	H_2O
Bond angle	**109°**	**107°**	**105°**

(iv) *Electronegativity of the atoms* **:** *If the electronegativity of the central atom decreases, bond angle decreases.*

	H_2O	$> H_2S$	$> H_2Se$	$> H_2Te$
Bond angle	104.5°	92.2°	91.2°	89.5°

In case the central atom remains the same, bond angle increases with the decrease in electronegativity of the surrounding atom, *e.g.*

	PCl_3	PBr_3	PI_3 ,	$AsCl_3$	$AsBr_3$	AsI_3
Bond angle	100°	101.5°	102°	98.4°	100.5°	101°

Example: Energy required to dissociate 4 grams of gaseous hydrogen into free gaseous atoms is 208 *kcal* at 25°C the bond energy of *H–H* bond will be **[CPMT 1989]**

(a) 104 *Kcal* (b) 10.4 *Kcal* (c) 20.8 *Kcal* (d) 41.6 *Kcal*

Answer: (a) 4 gram gaseous hydrogen has bond energy 208 *kcal*

So, 2 gram gaseous hydrogen has bond energy $= \frac{208}{2} kcal = 104\ kcal$.

Important Tips

- *More directional the bond, greater is the bond strength and vice versa. For example :*

$$sp^3-sp^3 > sp^2-sp^2 > sp-sp > p-p > s-p > s-s$$

- *The hybrid orbitals with more p-character are more directional in character and hence of above order.*
- *The terms 'bond energy' and 'bond dissociation' energy are same only for di-atomic molecules.*

- *The order of O–O bond length in O_2, H_2O_2 and O_3 is $H_2O_2 > O_2 > O_3$*
- *Because of higher electron density and small size of F atom repulsion between electron of it two F atoms, weakens the F-F bond.*
- *The bond length increases as the bond order decreases.*
- *Carbon monoxide (CO) has the highest bond energy(1070 $kJmol^{-1}$) of all the diatomic molecules. Bond energy of N_2(946$kJmol^{-1}$) and that of H_2(436 $kJmol^{-1}$) are other diatomic molecules with very high bond energies.*

VSEPR (Valence shell electron pair repulsion) theory.

The basic concept of the theory was suggested by **Sidgwick** and **Powell** (1940). It provides useful idea for predicting shapes and geometries of molecules. The concept tells that, the arrangement of bonds around the central atom depends upon the repulsion's operating between electron pairs(bonded or non bonded) around the central atom. **Gillespie** and **Nyholm** developed this concept as VSEPR theory.

The main postulates of VSEPR theory are

(i) For polyatomic molecules containing 3 or more atoms, *one of the atoms is called the central atom to which other atoms are linked.*

(ii) The geometry of a molecule depends upon the total number of valence shell electron pairs (bonded or not bonded) present around the central atom and their repulsion due to relative sizes and shapes.

(iii) If the central atom is surrounded by bond pairs only. It gives the symmetrical shape to the molecule.

(iv) If the central atom is surrounded by lone pairs (lp) as well as bond pairs (bp) of e^- then the molecule has a distorted geometry.

(v) *The relative order of repulsion between electron pairs is as follows : Lone pair-lone pair>lone pair-bond pair>bond pair-bond pair*

A lone pair is concentrated around the central atom while a bond pair is pulled out between two bonded atoms. As such repulsion becomes greater when a lone pair is involved.

Steps to be followed to find the shape of molecules :

(i) Identify the central atom and count the number of valence electrons.

(ii) Add to this, number of other atoms.

(iii) If it is an ion, add negative charges and subtract positive charges. Call the total *N*.

(iv) Divide N by 2 and compare the result with the following table and obtain the shape.

Total N/2	*Shape of molecule or ion*	*Example*
2	**Linear**	$HgCl_2$ / $BeCl_2$
3	**Triangular planar**	BF_3
3	**Angular**	$SnCl_2, NO_2$
4	**Tetrahedral**	CH_4, BF_4^-
4	**Trigonal Pyramidal**	NH_3, PCl_3
4	**Angular**	H_2O
5	**Trigonal bipyramidal**	PCl_5, PF_5
5	**Irregular tetrahedral**	SF_4, IF_4^+

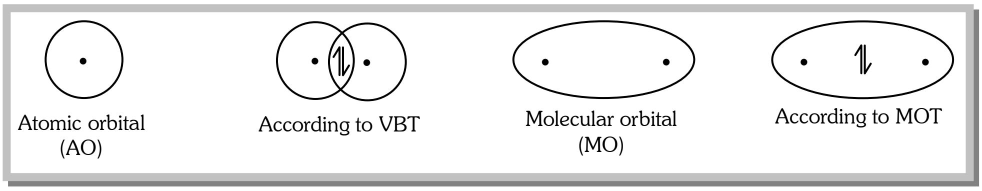
5	**T-shaped**	ClF_3, BrF_3
5	**Linear**	XeF_2, I_3^-
6	**Octahedral**	SF_6, PF_6
6	**Square Pyramidal**	IF_5
6	**Square planar**	XeF_4, ICl_4

Geometry of Molecules/Ions having bond pair as well as lone pair of electrons

Type of molecule	*No. of bond pairs of electron*	*No. of lone pairs of electrons*	*Hybridization*	*Bond angle*	*Expected geometry*	*Actual geometry*	*Examples*
AX_3	**2**	**1**	sp^2	**< 120°**	**Trigonal planar**	**V-shape, Bent, Angular**	**SO_2, $SnCl_2$, NO_2^-**
AX_4	**2**	**2**	sp^3	**< 109° 28′**	**Tetrahedral**	**V-shape, Angular**	**H_2O, H_2S, SCl_2, OF_2, NH_2^-, ClO_2^-**
AX_4	**3**	**1**	sp^3	**< 109° 28′**	**Tetrahedral**	**Pyramidal**	**NH_3, NF_3, PCl_3, PH_3, AsH_3, ClO_3^-, H_3O^+**
AX_5	**4**	**1**	sp^3d	**< 109° 28′**	**Trigonal bipyramidal**	**Irregular tetrahedron**	**SF_4, SCl_4, $TeCl_4$**
AX_5	**3**	**2**	sp^3d	**90°**	**Trigonal bipyramidal**	**T-shaped**	**ICl_3, IF_3, ClF_3**
AX_5	**2**	**3**	sp^3d	**180°**	**Trigonal bipyramidal**	**Linear**	**XeF_2, I_3^-, ICl_2^-**
AX_6	**5**	**1**	sp^3d^2	**< 90°**	**Octahedral**	**Square pyramidal**	**ICl_5, BrF_5, IF_5**
AX_6	**4**	**2**	sp^3d^2	**–**	**Octahedral**	**Square planar**	**XeF_4, ICl_4^-**
AX_7	**6**	**1**	sp^3d^3	**–**	**Pentagonal pyramidal**	**Distorted octahedral**	**XeF_6**

Molecular orbital theory.

Molecular orbital theory was given by **Hund** and **Mulliken** in 1932. When two or more constituent atomic orbital merge together, they form a bigger orbital called *molecular orbital* (MO). In atomic orbital, the electron is influenced by only one nucleus whereas in case of molecular orbital, the electron is influenced by two or more constituent nuclei. Thus, atomic orbital is monocentric and molecular orbital is polycentric. Molecular orbitals follow Pauli's exclusion principle, Hund’s rule, Aufbau's principle strictly.



The main ideas of this theory are : (i) When two atomic orbitals combine or overlap, they lose their identity and form new orbitals. The new orbitals thus formed are called **molecular orbitals**. (ii) Molecular orbitals are the energy states of a molecule in which the electrons of the molecule are filled just as atomic orbitals are the energy states of an atom in which the electrons of the atom are filled. (iii) In terms of probability distribution, a molecular orbital gives the electron probability distribution around a group of nuclei just as an atomic orbital gives the electron probability distribution around the single nucleus. (iv) *Only those atomic orbitals can combine to form molecular orbitals which have comparable energies and proper orientation*. (v) *The number of molecular orbitals formed is equal to the number of combining atomic orbitals*. (vi) When two atomic orbitals combine, they form two new orbitals called bonding molecular orbital and antibonding molecular orbital. (vii) *The bonding molecular orbital has lower energy and hence greater stability than the corresponding antibonding molecular orbital*. (viii) The bonding molecular orbitals are represented by σ, π etc, whereas the corresponding antibonding molecular orbitals are represented by σ^*, π^* etc. (ix) *The shapes of the molecular orbitals formed depend upon the type of combining atomic orbitals*.