

1. INTRODUCTION

A chemical bond is the physical process responsible for the attractive interactions between atoms and molecules, and that which confers stability to diatomic and polyatomic chemical compounds. In general, strong chemical bonding is associated with the sharing or transfer of electrons between the participating atoms. Molecules, crystals and diatomic gases—indeed most of the physical environment around us—are held together by chemical bonds, which dictate the structure of matter.

Bonds vary widely in their strength which is associated both with the energy required to break them, and the forces they exert on the atoms they hold together. Generally covalent and ionic bonds are often described as “strong”, whereas hydrogen bonds and van der Waal’s bonds are generally considered to be “weak,” although there exist overlaps in strength within these bond classes.

Since opposite charges attract via a basic electromagnetic force, the negatively-charged orbiting the nucleus and the positively-charged protons in the nucleus attract each other. Also, an electron positioned between two nuclei will be attracted to both of them. Thus, the most stable configuration of nuclei and electrons is one in which the electrons spend more time between nuclei, than anywhere else in space. These electrons cause the nuclei to be attracted to each other. However, this assembly cannot collapse to a size dictated by the volumes of these individual particles. Due to the matter wave nature of electrons and their relatively smaller mass, they occupy a very much larger amount of volume compared with the nuclei, and this volume occupied by the electrons keeps the atomic nuclei relatively far apart, as compared with the size of the nuclei themselves.

1.1 Cause of Chemical Combination

The atoms interact with each other on account of the following reasons :

- (i) **Decrease in energy :** It is a fundamental truth that all natural systems tend to lose potential energy and become more stable. Other things being equal, a system that has stored potential energy is less stable than a system that has none. It is an observed fact that a bonded state is more stable than unbonded state. This is due to the fact that the bonded state has lower potential energy than unbonded state. Hence, when two atoms approach each other, they combine only under the condition that there is a decrease in potential energy.

When two atoms approach each other, new forces of attraction and repulsion come into play. The forces of attraction are between the nucleus of one atom and the electrons of the other. The forces of repulsion are between two nuclei as well as between the electrons of the two atoms. If the net result is attraction, the total potential energy of the system decreases and a chemical bond results. No chemical bonding is possible if net result is repulsion.

- (ii) **Lewis octet rule :** The noble gases are known for their lack of chemical activity. There are no known compounds of helium, neon and argon. Why are these elements so unreactive

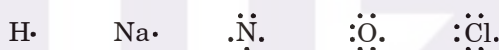
towards other elements ? All these elements have electronic structures that consist of filled outermost shells. Except for helium, whose electronic configuration is $1s^2$, the s-and p-subshells of the highest energy level contain a total of eight electrons. It is, therefore, concluded that s^2p^6 configuration in the outer energy level constitutes a-structure of maximum stability and therefore, of minimum energy.

The atoms of all elements when enter into chemical combination try to attain noble gas configuration, i.e., they try to attain either 2 electrons (when only one energy shell) or 8 electrons in their outermost energy level which is of maximum stability and hence of minimum energy. The tendency of atoms to achieve eight electrons in their outermost shell is known as Lewis octet rule. Octet rule was the basis of electronic theory of valency.

1.2 Lewis Symbols of Elements

Chemical bonding mainly depends on the number of electrons present in the outermost energy level. These electrons are termed as valency electrons. The electronic configuration of sodium (Na) is 2, 8, 1 and that of sulphur has (S) 2, 8, 6. Thus, sodium has one valency electron while sulphur has six valency electrons.

The valency electrons in atoms are shown in terms of Lewis symbols. To write Lewis symbol for an element, we write down its symbol surrounded by a number of dots of crosses equal to the number of valency electrons. Paired and unpaired valency electrons are also indicated. The Lewis symbols for hydrogen, sodium, nitrogen, oxygen and chlorine may be written as :



Generalised, 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 | $\text{X}\cdot$ | $\cdot\text{X}\cdot$ | $\cdot\ddot{\text{X}}\cdot$ | $\cdot\ddot{\text{X}}\cdot$ | $\cdot\ddot{\text{X}}\cdot$ | $\cdot\ddot{\text{X}}\cdot$ | $:\ddot{\text{X}}:$ |

1.3 Electronic theory of Valency

The theory of valency explains chemical combination in terms of electrons. The theory was developed independently by W. Kossel and G.N. Lewis (1916) and extended by Irving Langmuir (in 1919).

The chemical behaviour of an atom is determined to a large extent by the number and arrangement of electrons in the outer orbitals of the atom. Only these electrons are involved in chemical combination and so these are called the **valence electrons**.

Completed Electron Octet or Duplet

Group 0 of the periodic table contains the noble gases. With the exception of helium which has a $1s^2$ electron arrangement others have $ns^2 np^6$ configuration in the outer orbitals.

| | |
|----|--|
| He | $1s^2$ |
| Ne | $1s^2 2s^2 2p^6$ |
| Ar | $1s^2 2s^2 2p^6 3s^2 3p^6$ |
| Kr | $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$ |
| Xe | $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6$ |

Since the atoms of the noble gases were not known to form chemical bonds, it was argued that the presence of 8 electrons (an electron octet) in the valence shell makes the atom stable. Therefore all other atoms must undergo bonding by gaining or losing or sharing electrons so as to acquire the electronic configuration of the nearest inert gas. The presence of 8 electrons gives the name **octet rule** to this concept. In the case of the first few elements such as hydrogen, lithium and beryllium the atoms combine in such a way as to attain the stable structure of helium with 2 electrons (duplet) in its only one valence shell. There are, however, many exceptions to the octet rule. Also compounds of noble gases, especially xenon, have been synthesized.

Hence, bond formation can take place in 3 ways.

- (1) By losing or accepting electrons as known as electrovalent bond.
- (2) By equal contribution of electrons from two atoms and these electrons are then shared equally to form covalent bond.
- (3) Contribution is made by one atom and both the electrons are shared equally by 2 atoms to form co-ordinate bond.

Thus it can be summarised as “The union of two or more atoms involving redistribution of electrons in their outer shells (either by transference or sharing) in such a way so that all the atoms acquire the stable noble gas configuration of the minimum energy is known as **electronic theory of valency**”.

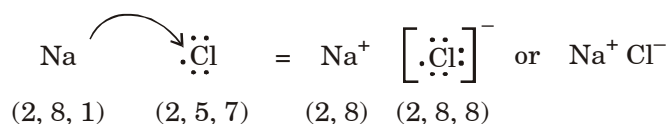
2. IONIC BOND

An **Ionic bond** is a type of chemical bond that involves a metal and a non-metal ion through electrostatic attraction. In short, it is a bond formed by the attraction between two oppositely charged ions. The metal donates one or more electrons, forming a positively charged ion or cation with a stable electron configuration. These electrons then enter the non metal, causing it to form a negatively charged ion or anion which also has a stable electron configuration. The electrostatic attraction between the oppositely charged ions causes them to come together and form a bond.

For example :

Sodium Chloride : The free sodium atom has one valence electron (electronic configuration 2, 8, 1) i.e. $3s^1$. Whereas the chlorine atom has seven valence electrons (electronic configuration 2, 8, 7) i.e. $3s^2 3p^5$. In forming an ionic bond, the sodium atom loses its valence electron which is accepted by chlorine atom. As a result sodium achieves noble gas configuration of Neon (2, 8) and becomes positive ion (Na^+) chlorine achieves noble gas configuration of argon (2, 8, 8) and acquires a negative charge (Cl^-). The attraction between sodium ion and chloride ion is an ionic bond.

A short hand way of showing the formation of sodium chloride using dot symbols.

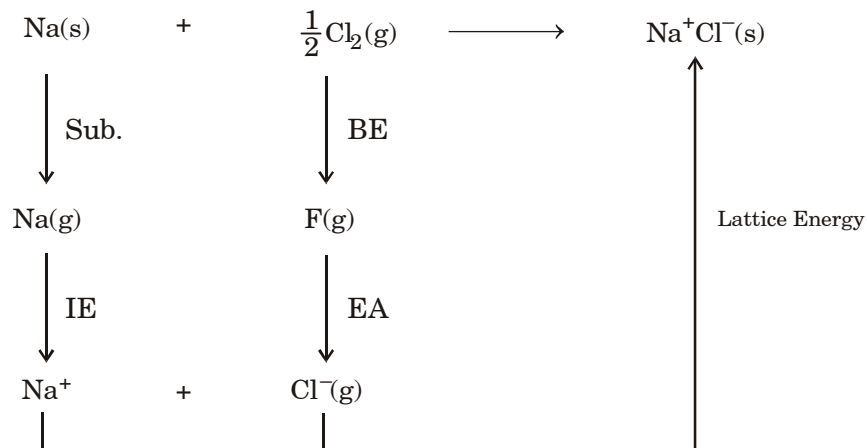


Conditions for Forming Electrovalent or Ionic Bond

The following conditions favour the formation of an electrovalent bond.

- (i) **Number of valency electrons :** One atom should possess 1, 2 or 3 valency electrons while the other atom should have 5, 6 or 7 valency electrons. Thus, they can also form electrovalent bonds but do not acquire inert gas configuration always.
- (ii) **Difference in electronegativity :** The formation of an electrovalent bond will be easier if the difference in the electronegativities of the two atoms is high. A difference of about 2 is necessary for the formation of an electrovalent bond. The electronegativity of sodium is 0.9 and that of fluorine is 4.0. Since the difference is 3.1 both will readily form an electrovalent bond.
- (iii) **Overall decrease in energy :** In the formation of an electrovalent bond, there must be overall decrease in energy, i.e., energy must be released. Energy changes are involved in the following steps :

This is called as **Born-Haber cycle**.



Where ΔH_{sub} is the sublimation energy, BE is the bond energy, IE is ionization energy and EA is electron affinity.

- (1) **Sublimation Energy** : The energy required to convert one mole of a solid into gas at constant pressure and temperature.
- (2) **Ionization energy** : The energy required by the metal atom to release its valence electron. For example, sodium requires small energy to give up its loosely field electron and form Na^+ ion.

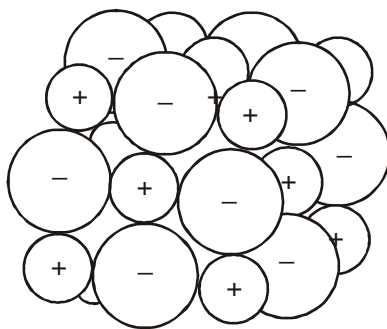
Ionization energy of an element with a single electron in its valence still is less than that with two electrons. In going across a period of the periodic table from left to right, I.E. increases and the formation of the cation is less likely. On going down a group, the outermost electron gets further away from the nucleus, and hence is more easily removed i.e. I.E. decreases, the formation of the cation becomes more likely lower the value of ionisation energy of an atom, greater will be the ease of formation of the cation from it.

- (3) **Bond energy** : The energy required required to break the molecule into atoms is called bond energy or dissociation energy.
- (4) **Electron affinity** : the amount of energy released when an atom takes up an electron and forms an anion. For example, chlorine takes up an electron from the Na atom and forms Cl^- ion. Non-metals of groups VIA and VIIA have high electron affinity and can form ionic bonds.

In going across a period from left to right, electron affinity (energy released) increases and so the formation of negative ion becomes more likely. On going down a group, electron affinity decreases and so the formation of anion becomes less likely.

Thus Higher the value of electron affinity of the atom, greater the ease of formation of the anion form it, i.e., other atom should have high value of electron affinity.

- (5) **Lattice energy** : Cation and anion attract each other by electrostatic force of attraction to give a molecule A^+B^- . Since the electrostatic field of a charged particle extends in all



Crystals of ionic compounds

directions, a positive ion is surrounded by a number of negatively charged ions while each negative ion similarly surrounded by a number of positive ions. These cations and anions arrange systematically in an alternating cation-anion pattern as shown in Fig. This is called a crystal lattice. This process of clustering ions increases the force of attraction and thus potential energy decreases. The energy released when the requisite number of positive and negative ions are condensed into crystal to form one mole of the compound is called lattice energy.

The value of lattice energy depends on the charges present on the two ions and the distance between them. According to Coulomb's law, the force of attraction (F) between two oppositely charged ions in air with charges equal to q_1 and q_2 and separated by a distance d is given by,

$$F = \frac{1}{4\pi\epsilon_0 K} \frac{q_1 q_2}{d^2}$$

where d is equal to sum of ionic radii of the two ions and K is dielectric constant of medium.

$$F = \frac{1}{4\pi\epsilon_0 K} \frac{q_1 q_2}{(r_{A^+} + r_{B^-})^2}$$

The value of F increases if (i) q_1 and q_2 are high and (ii) $(r_{A^+} + r_{B^-})$ is small.

The stability of the ionic compound and the strength of the ionic bond depends on the value of F . Higher than value of F , greater shall be the stability of the ionic compound and hence greater shall be the strength of the ionic bond. For example, NaCl is more stable than CsCl as $(r_{Cs^+} + r_{Cl^-})$ is less than $(r_{Na^+} + r_{Cl^-})$. MgO is more stable than NaCl as the product $q_1 q_2$ is four times more in MgO than NaCl.

Conclusions :

- (i) An ionic bond is purely electrostatic in nature.
- (ii) Its formation is favoured by :
 - (a) **Low ionisation potential (I.P.)** of the element that forms a cation on losing electron(s). The element should be metal, i.e., electropositive in nature.
 - (b) **High electron affinity (E.A.)** of the element that forms an anion on gaining electron(s). The element should be non-metal, i.e., electronegative in nature.
 - (c) **High lattice energy (L.E.)** : The energy release when isolated ions form a crystal. The value of lattice energy depends on the charges present on the two ions and distance between them. It shall be high if charges are high and ionic radii are small.
 - (d) The summation of three energies should be negative, i.e., energy is released.

$$\text{I.P.} + \text{E.A.} + \text{L.E.} = -\text{ive}$$

(iii) Greater the difference of electronegativity between two atoms, higher will be the possibility of ionic bond formation.

(iv) Electrovalency

The capacity of an element to form electrovalent or ionic bond is termed as electrovalency. The capacity is measured in terms of the electrons lost or accepted. Thus, electrovalency of an element is equal to the number of electrons lost by an atom of the element or gained by the atom of the element as to acquire inert gas configuration. The elements which lose electron or electrons show positive electrovalency and the elements which gain electron or electrons show negative electrovalency. Generally positive and negative signs are not used in practice and only the number is taken to represent electrovalency.

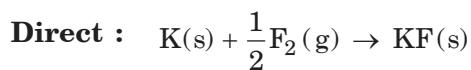
| Element | No. of electrons lost or gained by an atom | Electrovalency | Change in electronic configuration |
|---------|--|----------------|---|
| Na | 1 (lost) | 1 (Monovalent) | 2, 8, 1 to 2, 8 (Na^+) |
| K | 1 (lost) | 1 (Monovalent) | 2, 8, 8, 1 to 2, 8, 8 (K^+) |
| Mg | 2 (lost) | 2 (Divalent) | 2, 8, 2 to 2, 8 (Mg^{++}) |
| Ca | 2 (lost) | 2 (Divalent) | 2, 8, 8, 2 to 2, 8, 8, (Ca^{++}) |
| Al | 3 (lost) | 3 (Trivalent) | 2, 8, 3 to 2, 8 (Al^{+++}) |
| F | 1 (gained) | 1 (Monovalent) | 2, 7, to 2, 8 (F^-) |
| Cl | 1 (gained) | 1 (Monovalent) | 2, 8, 7 to 2, 8, 8 (Cl^-) |
| O | 2 (gained) | 2 (Divalent) | 2, 6 to 2, 8 (O^{--}) |
| S | 2 (gained) | 2 (Divalent) | 2, 8, 6 to 2, 8, 8 (S^{--}) |
| N | 3 (gained) | 3 (Trivalent) | 2, 5 to 2, 8 (N^{---}) |

3. Determination of lattice energy

The lattice energy of an ionic solid is determined experimentally by a process known as Born-Haber cycle. According to this theory following steps are involved :

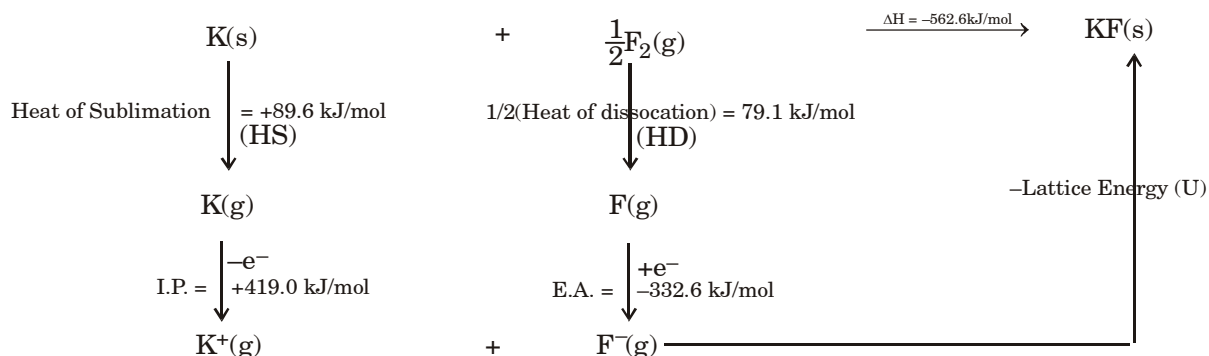
- The reactant are converted into gaseous state.
- The gaseous atoms are converted into ions.
- The gaseous ions are combined to form ionic compound.

For example the formation of KF can occur either directly or in steps.



$$\Delta H \text{ or heat of formation} = - 562.6 \text{ kJ/mol}$$

Steps :



On the basis of above cycles (or constant heat summation rule)

Heat of formation = Heat of atomization + Heat of dissociation + I.P. + E.A. + Lattice Energy

$$\Delta H = \text{HS} + \frac{\text{HD}}{2} + \text{I.P.} + (\text{E.A.}) + (-U)$$

$$-562.6 = 89.6 + 79.1 + 419.0 - 332.6 - U$$

$$U = 817.7 \text{ kJ/mol}$$

$$\text{Lattice energy of KF} = -U = -817.7 \text{ kJ/mol}$$

Method of Writing Formula of an Ionic Compound

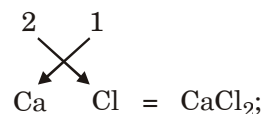
In order to write the formula of an ionic compound which is made up of two ions (simple or polyatomic) having electrovalencies x and y respectively, the following points are followed:

- Write the symbol 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.
- Write their electrovalencies in figures on the top of each symbol as $A^x B^y$.
- Divide their valencies by H.C.F.

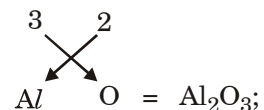
- Now apply criss cross rule as $\begin{array}{cc} x & y \\ \swarrow & \searrow \\ A & B \end{array}$ i.e., formula $A_y B_x$.

Examples :

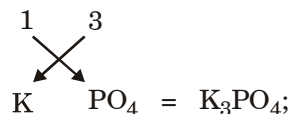
Calcium chloride



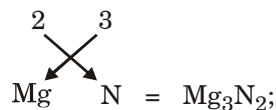
Aluminium oxide



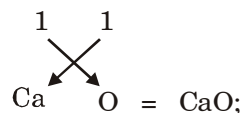
Potassium phosphate



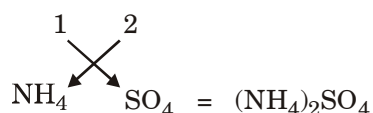
Magnesium nitride



Calcium oxide



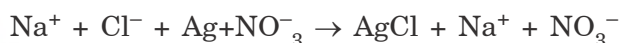
Ammonium sulphate



General Characteristics of Ionic Compounds

- (i) Generally ionic compounds are hard solids. As single ions of a metal are not associated in the solid with single ions of a non-metal, separate units of ionic compounds do not exist. It is, therefore, wrong to talk of a molecule of an ionic compound. The formula only indicates the ratio of number of ions and the crystal consists of a very large number of oppositely charged ions. Thus in NaCl crystal each Na^+ ion is surrounded by 6 Cl^- ions and vice versa (in an octahedral arrangement). The attraction between Na^+ and Cl^- ions is quite large.
- (ii) As a good deal of thermal energy is required to overcome the large electrostatic forces of attraction in an ionic crystal, ionic compounds have high melting and boiling points.
- (iii) Ionic compounds are commonly soluble in water and other polar solvents (which separate the ions). They are practically insoluble in organic solvents such as benzene, carbon tetrachloride, etc., as there is no attraction between ions and the molecules of the non-polar liquids.
- (iv) Ionic compounds are electrolytes. In the presence of a ionizing solvent such as water, the electrostatic forces between the ions are so greatly reduced that the ions get separated. (This is due to the electrostatic attraction between the ions and the polar molecules of the solvent.) The free ions in solution conduct electricity and on passing a current, the ionic compound undergoes chemical decomposition (called electrolysis). When an ionic compound is melted, the crystal lattice structure is broken and free ions are produced. It is the free movement of ions which makes an ionic compound a conductor and to undergo electrolysis in the molten condition.

- (v) When an ionic compound dissolves in water, the ions get solvated (in this case hydrated). The energy released is called solvation energy. Insoluble ionic compounds (eg., sulphates, phosphates and fluorides of Ca, Sr and Ba) have very high lattice energies and the solvation energy of the constituent ions is insufficient to counteract the high lattice energies and make them soluble.
- (vi) The chemical properties of an ionic compound are the properties of its constituent ions. Thus all chlorides give the characteristic reactions of the chloride ion (reactions with conc. H_2SO_4 , AgNO_3 solution, etc.). All acids which contain H^+ ions give the same reactions (change blue litmus to red, effervesce with a carbonate, etc.).
- (vii) Reactions between solutions of ionic compounds are almost instantaneous, because they are reactions between ions (and do not involve the breaking up of bonds as in covalent compounds, q.v.). For example, when silver nitrate solution is added to sodium chloride solution, silver chloride is immediately precipitated. The reactions may be represented thus :



Variable Electrovalency

Certain elements (metals) show more than one electrovalency in their electrovalent compounds. The atoms of these elements lose different number of electrons under different conditions, thereby showing variable electrovalency. The following are two reasons for variable electrovalency :

- (i) **Instability of the core :** The residue configuration left after the loss of valency electrons (electrons present in the outermost energy level) is called a core or kernel. 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 $ns^2 np^6$ but $ns^2 np^6 d^{1 \text{ to } 10}$. The outershell generally loses one or more electrons giving rise to metal ions of higher valencies. The variable valencies of iron can be explained on this basis.

| | | | |
|------------------|----|----------------|---------------------------|
| Fe | 26 | 2, 8, 8 + 6, 2 | $3s^2 3p^6 3d^6, 4s^2$ |
| Fe^{2+} | 24 | 2, 8, 8 + 6 | $3s^2 3p^6$ (Not stable) |
| Fe^{3+} | 23 | 2, 8, 8 + 5 | $3s^2 3p^6 3d^5$ (Stable) |

Thus, iron shows +2 and +3 valencies. The compounds, in which iron is in trivalent state, i.e., ferric compounds are more stable than the compounds in which iron is in divalent state (ferrous compounds).

- (ii) **Inert pair effect :** some of heavier representative elements of third, fourth and fifth groups having configurations of the 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 on 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. A partial explanation of the inert pair effect is due to the fact that outer ns^2 electrons penetrate to some extent to penultimate orbit consisting 18 electrons thereby attracted strongly towards nucleus. Inert pair effect increases in a group as the atomic number increases.

| | | | |
|------------------|-------------|-------------------------------|----------------------------|
| Tl | (III group) | 2, 8, 18, 32, 18, $6s^2 6p^1$ | |
| Tl ⁺ | | 2, 8, 18, 32, 18, $6s^2$ | Only 6p electron is lost |
| Sn | (IV group) | 2, 8, 18, $5s^2 5p^2$ | |
| Sn ²⁺ | | 2, 8, 18, 18, $5s^2$ | Only 5p electrons are lost |
| Pb | (IV group) | 2, 8, 18, 32, 18, $6s^2 6p^2$ | |
| Pb ⁺ | | 2, 8, 18, 32, 18, $6s^2$ | Only 6p electrons are lost |
| Bi | (V group) | 2, 8, 18, 32, 18, $6s^2 6p^3$ | |
| Bi ³⁺ | | 2, 8, 18, 32, 18, $6s^2$ | Only 6p electrons are lost |

When sufficient energy is available, the s-electrons also enter into bond formation and higher valencies are observed. This tendency to show higher valencies is less in the case of Tl, Pb and Bi but more in the case of comparatively lighter elements such as In, Sn, Sb, etc.

4. COVALENT BONDING

Certain elements which have high ionisation energies are incapable of transferring electrons and other having low electrons affinities, fail to take up electrons. The atoms of such elements share their electrons with the atoms of other elements (and sometimes among themselves) in such a manner that both the atoms form complete outer shell. In this manner they achieve stability. Such an association through sharing of electron pairs among atoms of different or of same kinds is known as Covalent Bond. This was proposed by G.N. Lewis.

The covalent bonding can be achieved in two ways :

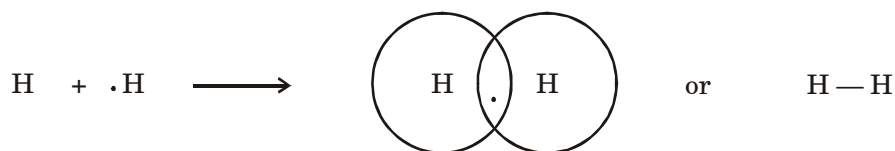
- Sharing electrons between atoms of same kinds, formation of H_2 , Cl_2 , O_2 etc.
- sharing of electrons between atoms of different kinds, formation of HCl , CO_2 , H_2O , CH_4 etc.

The bond is, non-polar bond.

Covalent bond may be single, double or a triple bond. Double and triple covalent bonds are called multiple covalent bonds. Single covalent bond is formed by sharing of only one electron pair. This bond is represented by single dash (—). Double and triple covalent bonds are formed when atoms bonded together shared two or three electron pair, respectively. These bonds are represented by double dash (=) and triple dash (≡) respectively. Some examples of covalent bonding are given below :

1. Formation of hydrogen molecule :

In the formation of hydrogen molecule, each hydrogen atom contributes one electron and then the pair is shared between two atoms. Both the atoms acquire stable configuration of helium. Thus, the molecule consists of one single covalent bond.

2. Formation of F_2 and other like molecules

It is formed by combination of two F atoms by sharing one electron each. It is represented by Lewis dot structure as follows :

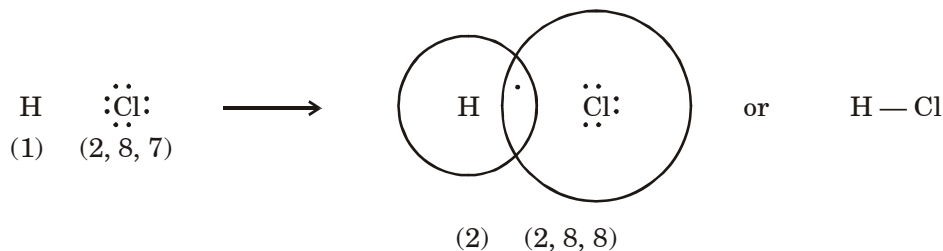


Lewis dot structure shows only the electrons of outer most shell. Note that both of F atoms now have 8 electrons each in their outer shell.

Note : Pair of electrons depicted as $\cdot\cdot$ or xx is called as lone pair (lp) and that by $\text{x}\cdot$ is called as shared pair or bonded pair (bp). Lone pair is the pair of electrons belonging to one atom only.

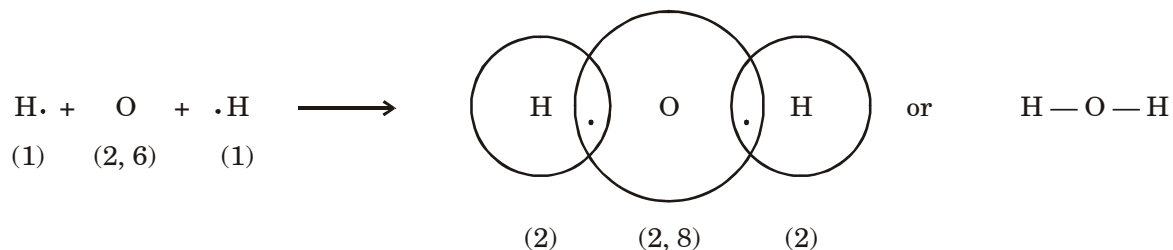
3. Formation of HCl molecules

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.



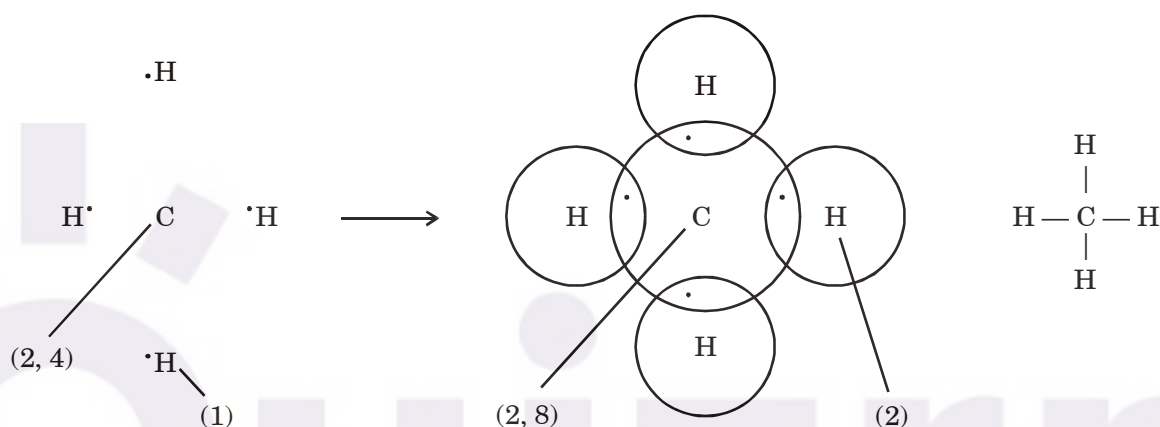
4. Formation of water molecule

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



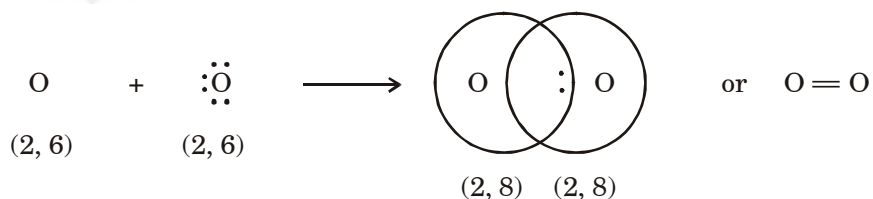
5. Formation of methane

Carbon has four electrons in the valency shell. It can achieve stable configuration of neon by sharing four electrons with four hydrogen atoms, one with each hydrogen atom. Each hydrogen atom acquires helium configuration.



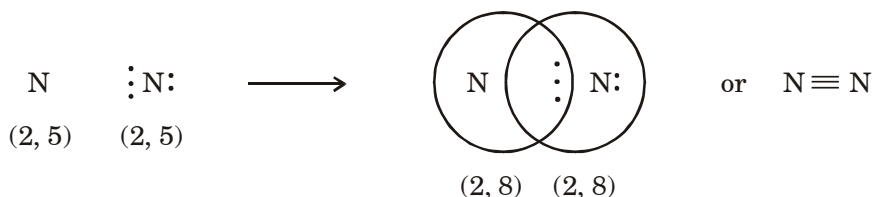
6. Formation of O₂ molecules

Each oxygen atom contributes two electrons and two pairs of electrons are then shared equally. Both the atoms acquire configuration of neon.



7. Formation of N₂ molecules

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.



Covalency

It is defined as the number of electrons contributed by an atom of the element for sharing with other atoms as to achieve noble gas configuration. It can also be defined as the number of covalent bonds formed by the atom of the element with other atoms. The usual covalency of an element except hydrogen (which has covalency 1) is equal to (8-group number of Mendeleeff's table to which an element belongs). This is true for the elements belonging to IV, V, VI and VII groups.

| Element | Group | (8-Group number) | Covalency |
|---------|-------|------------------|-----------|
| C | IV | $8 - 4 = 4$ | 4 |
| Si | IV* | $8 - 4 = 4$ | 4 |
| N | V | $8 - 5 = 3$ | 3 |
| P | V | $8 - 5 = 3$ | 3 |
| O | VI | $8 - 6 = 2$ | 2 |
| S | VI | $8 - 6 = 2$ | 2 |
| F | VII | $8 - 7 = 1$ | 1 |
| Cl | VII | $8 - 7 = 1$ | 1 |

Generally, the covalency of an element is equal to the total number of unpaired electrons in s- and p-orbitals of the valency shell.

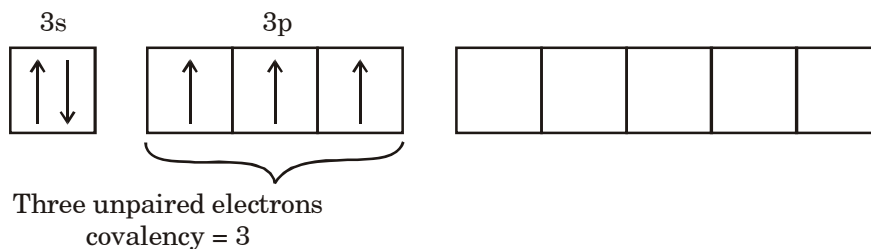
| | | |
|---|----------------------------------|------------------|
| Hydrogen has one unpaired orbital | <div>1s</div> <div>↑</div> | Covalency One |
| Fluorine has only one unpaired orbital | <div>↑↓</div> <div>↑↓ ↑↓ ↑</div> | One |
| Oxygen has two unpaired p-orbitals | <div>↑↓</div> <div>↓↑ ↑ ↑</div> | Two |
| Nitrogen has three unpaired p-electrons | <div>↑↓</div> <div>↑ ↑ ↑</div> | Three |

These four elements do not possess d-orbitals in their valency shell. However, the elements having vacant d-orbitals in their valency shell like P, S, Cl, Br, I, show variable covalency by increasing the number of unpaired electrons under excited conditions, i.e., unpairing the paired orbitals and

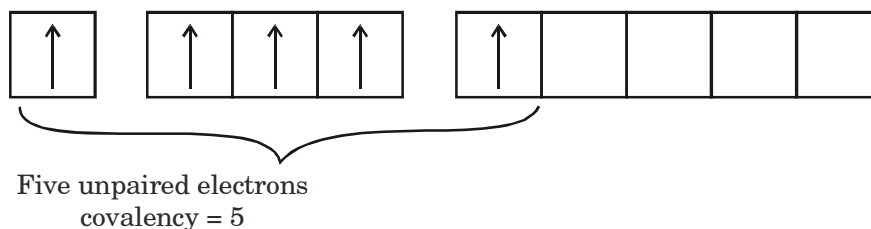
shifting the electrons to vacant d-orbitals. [Such a shifting is not possible in the case of H, N, O and F because d-orbitals are not present in their valency shell.]

Phosphorus shows 3 and 5 covalencies.

Phosphorus atom in ground state

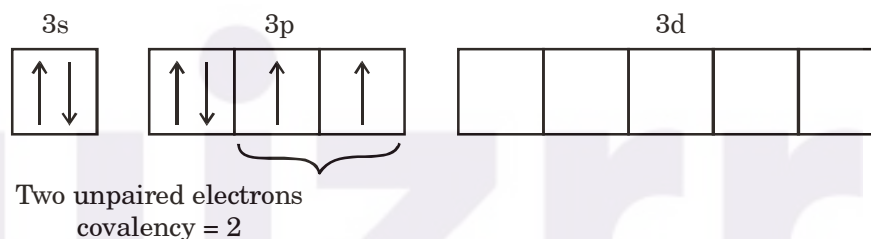


Phosphorus atom in excited state



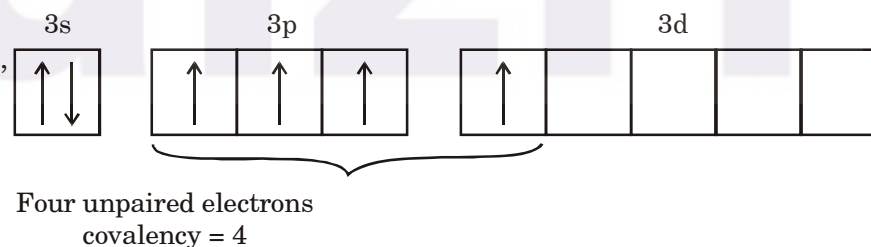
Sulphur atoms shows 2, 4 and 6 covalencies.

Sulphur atom in ground state

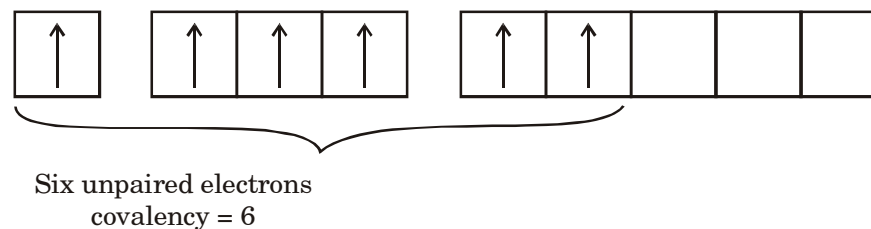


Sulphur atom in excited state,

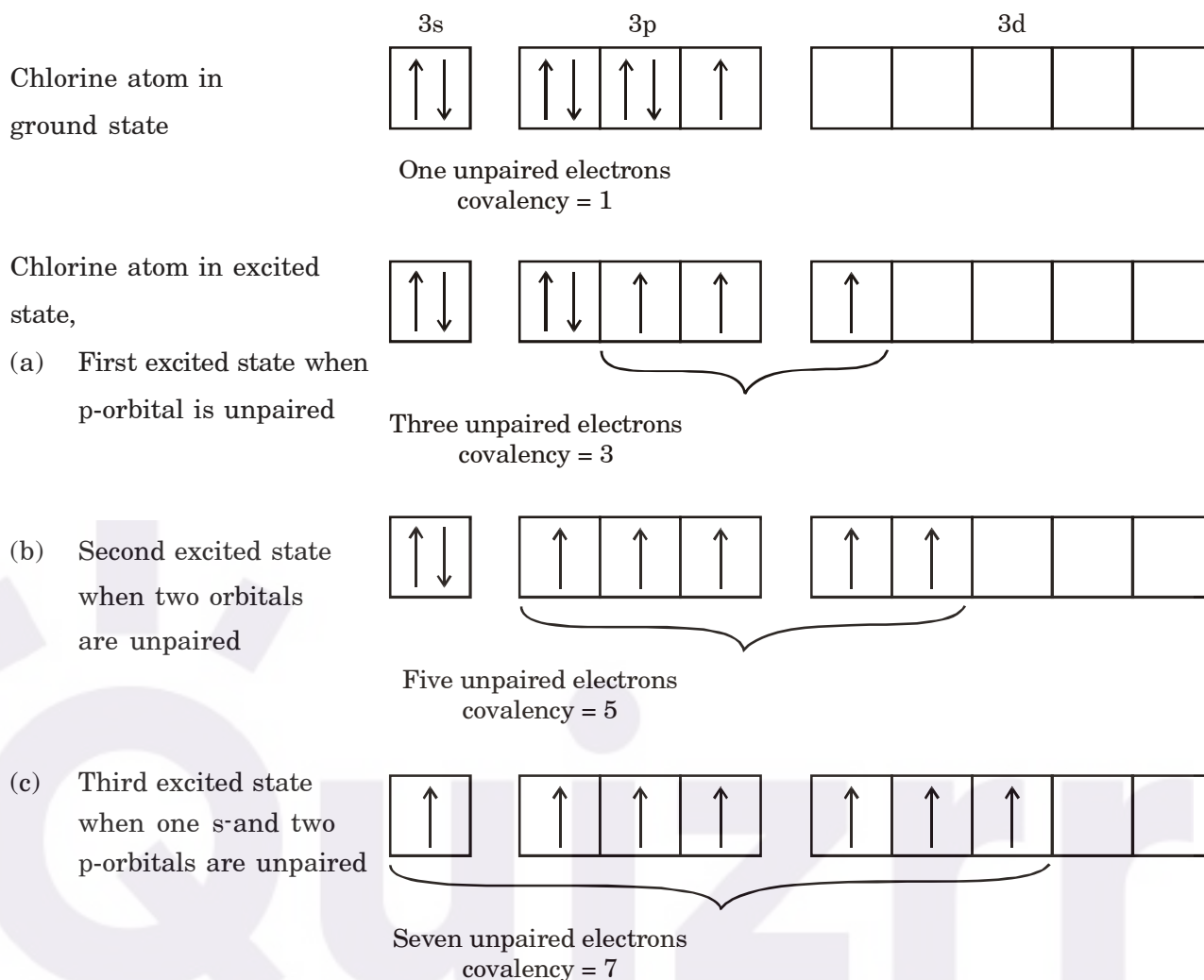
- (a) When p-orbital is unpaired
(first excited state.)



- (b) When s-and p-orbital is unpaired
(first excited state).



Chlorine shows 1, 3, 5 and 7 covalencies.



Thus, variable covalency is shown by those elements whose atoms have vacant d-orbitals in their valency shell.

General Characteristics of Covalent Compounds

- (i) In a purely covalent compound the electrons in the bond are shared equally between the atoms linked by the bond; the resultant particles formed are not electrically charged. So, separate molecules of the covalent compounds exist. Covalent compounds may therefore be expected to be gases or low boiling liquids or soft, low melting solids at ordinary temperature. In the solid state they may be amorphous or present as molecular crystals the molecules being held together by what are called weak van der Waals forces of attraction.
- (ii) Since the molecules are held together by weak van der Waals forces, covalent compounds (except those consisting of giant molecules) have low melting and boiling points; very little thermal energy is needed to overcome these weak intermolecular forces.

- (iii) They are non-electrolytes, i.e., they do not contain ions. Even in giant molecules such as diamond there are no free electrons. So they are very poor conductors of electricity.
- (iv) They are generally soluble in organic (non-polar) solvents such as benzene or carbon tetrachloride but are insoluble in water or other ionizing solvents. (The solubility of covalent compounds is very much dependent on the size of the molecules; giant molecules are practically insoluble in nearly all solvents.)
- (v) Reactions between covalent compounds are slow and often incomplete and reversible. This is so because the reaction involves breaking and making of bonds i.e., energy considerations are involved for reactants, activated complexes and products.
- (vi) A covalent bond is a space-directed bond and it may exhibit isomerism.

Polar Covalent Bonds – Electronegativity

The shared pair of electrons may be shared equally between two atoms; then the covalent bond is said to be non-polar. Equal sharing occurs between identical atoms, as in $\text{H} - \text{H}$ or $\text{Cl} - \text{Cl}$ (i.e., in homonuclear molecules) or between identical atoms with identical neighbours as in $\text{H}_3\text{C}-\text{CH}_3$. When the two bonded atoms are dissimilar (i.e., in heteronuclear molecules) the sharing is unequal. For example a chlorine atom has a greater electron attracting power than a hydrogen atom; so in $\text{H} - \text{Cl}$, the shared pair of electrons are drawn more towards chlorine and away from hydrogen. The result is separation of charges within the molecule, the chlorine end acquiring a slight negative charge and the hydrogen end a slight but equal positive charge $\overset{\delta+}{\text{H}}-\overset{\delta-}{\text{Cl}}$. Such covalent bonds are said to be polar (i.e. bonds formed by sharing a pair of electrons between two atoms but displaced towards the nucleus of one of the bonded atoms).

The net tendency of a bonded atom in a covalent to attract the shared pair of electrons towards itself is known as electronegativity. (This word does not mean the actual content of the electric charge, but just the tendency to acquire it in a molecule). Thus F is highly electronegative, but F^- which has already an extra electron is not.

To assess the tendency of an atom of a given element to attract electrons towards itself in a covalent bond, relative electronegativity values are used.

- (i) Electronegativity value increase across a period and decrease down a group.
- (ii) Smaller atoms have greater electronegativity than larger ones and so they attract electrons more towards them than larger ones. Alkali metals have low electronegativities and halogens high electronegativities.
- (iii) Atoms with nearly filled shells of electrons (e.g., halogens) have greater electronegativity than those with sparsely occupied shells.

- (iv) Elements with low electronegativity values such as Cs (0.8) and Rb (0.8) tend to form positive ions, i.e., these are metals. Elements with high electronegativity values such as F(4.0) and O (3.5) tend to form negative ions, i.e., these are non-metals.
- (v) Electronegativity value may be used to make rough predictions of the type of bonding to be found in a compound. The larger the difference between electronegativity values of two combining atoms, the more polar the covalent bond. If the difference is greater than 2, the greater the chance for ionic bonding (i.e., the chance of covalent bond assuming 100% ionic character). From this point of view ionic may be considered to be an extreme case of a polar bond (with total separation of charges).

If the difference between the electronegativities of the combining atoms is zero or small, the bond is essentially non-polar.

Let X_A and X_B represent the electronegativities of two atoms A and B. If $X_B - X_A = 1.7$, the covalent bond A – B is said to have 50% ionic character. On the basis, the % ionic character in some typical bonds are calculated (Table). These calculations are very qualitative.

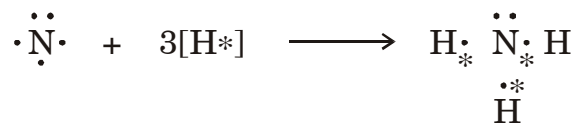
% Ionic Character of Bonds

| | | | |
|--------------|---------------|--------------|--------------|
| C – H 4% | N – H 10% | O – H 39% | F – H 60% |
| C – F 43% | C – Cl 11% | C – Br 3% | C – I 0% |

5. THE LEWIS THEORY

The octet rule : The Lewis theory gave the first explanation of a covalent bond (in terms of electrons) that was generally accepted. If two electrons are shared between two atoms, this constitutes a bond and binds the atoms together. For many light atoms, a stable arrangement is attained when the atom is surrounded by eight electrons.

This octet can be made up from some electrons which are totally owned and some electrons which are 'shared'. Thus atoms continue to form bonds until they have made up an octet of electrons. This is called the '**octet rule**'. The octet rule explains the observed valencies in a large number of cases. For example nitrogen atom has 5 outer electrons and in NH_3 it shares three of these, forming three bonds and thus attaining an octet, hydrogen has only one electron and by sharing one electron of two electrons.

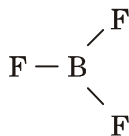


Exception to octet rule

It is observed that atoms in some molecules could exist with some other number of electrons in their valence shells, rather than 8 electrons without affecting the stability. We are discussing some of them.



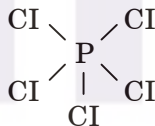
Boron atom has only six electrons in its outershell even after making three single bonds with three F atoms (i.e. it completes only sixet).



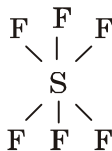
Beryllium has only four electrons in its outershell even after making two single bonds with two Cl atoms.



Phosphorus after making five single bonds with five Cl atoms has ten electrons in its outershell.



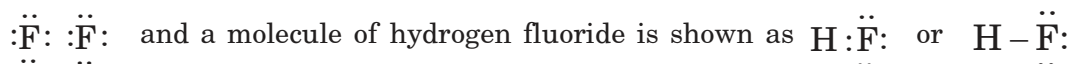
Sulphur makes six single bonds with six F atoms and thus has 12 electrons in its outershell.



Lewis Structures of Molecules

The formula of a molecule shows the number of atoms of each element but does not show the bonding arrangement of the atoms. To represent the bonding pattern in a molecule, the electron

dot symbols of the elements are arranged such that the shared pairs and unshared pairs (called lone pairs) are shown and the octet rule (or duet for hydrogen) is satisfied. For example, a molecule of fluorine is shown as

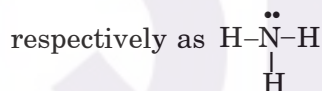


Arrangement of dot symbols used to represent molecules are called Lewis Structures. Lewis structures do not convey any information regarding the shape of the molecule. Usually, the shared pairs of electrons are represented by lines between atoms and any unshared pairs are shown as dot pairs.

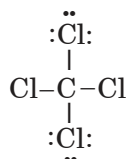
Lewis structures are written by fitting the element dot symbols together to show shared electron pairs and to satisfy the octet rule. For example,

(i) In water (H_2O), one H and two $\cdot\ddot{\text{O}}\cdot$ complete their duet and octet respectively as $\begin{array}{c} \ddot{\text{O}} - \text{H} \\ | \\ \text{H} \end{array}$

(ii) In ammonia (NH_3), three $\cdot\text{H}\cdot$ and one $\cdot\ddot{\text{N}}\cdot$ fit together and satisfy their duet and octet



(iii) In carbon tetrachloride (CCl_4), four $:\ddot{\text{Cl}}:$ and $\cdot\ddot{\text{C}}\cdot$ complete their octet as



For the given molecules, we have adopted hit & trial to fit the dot symbols together and satisfy the octet rule. But remember that hydrogen form one bond, oxygen forms two bonds, nitrogen three bonds and carbon forms four bonds. For simpler molecules, the hit & trial method works perfectly but for slightly complicated polyatomic species, this may give us more than one possible structure. Thus, a systematic approach is needed to design the Lewis structures of such polyatomic species. But before proceeding further, let us understand the limitation of this approach.

Limitations of Lewis Theory of Drawing Structure

- (i) This method would be applicable to only those molecules/species, which follow octet rule except hydrogen.
- (ii) This method would not be applicable to species, which have more than one central atom (like N_2O_4 , N_2H_4 etc.).
- (iii) This method is also not suitable for species, which contains transition metal atom as the central atom.

There are three kinds of molecules/species, which do not follow octet rule.

- (a) Molecules, which have contraction of octet. Such molecules are electron deficient. For example, BH_3 , BF_3 , BCl_3 , AlCl_3 , GaCl_3 etc.
- (b) Molecules, which have expansion of octet. Such species have more than eight electrons in their outermost shell. This is possible in those molecules, which have vacant d-orbitals, thus they can expand their octet. For example, PCl_5 , SF_6 etc.
- (c) Molecules containing odd number of electrons (in total) cannot satisfy octet rule. Such species are called odd electron species and are paramagnetic in nature due to presence of unpaired electron. For example, NO , NO_2 and ClO_2 .

Method of Drawing Lewis Structures

To draw the Lewis structures of polyatomic species, follow the given sequence.

- (i) First calculate n_1 .

n_1 = Sum of valence electron of all the atoms of the species \pm net charge on the species.

For a negatively charged species, electrons are added while for positively charged species, the electrons are subtracted. For an uninegatively charged species, add 1 to the sum of valence electrons and for a dinegatively charged species, add 2 and so on.

- (ii) Then calculate n_2 .

$n_2 = (8 \times \text{number of atoms other than H}) + (2 \times \text{number of H atoms})$

- (iii) Subtract n_1 from n_2 , which gives n_3 .

$n_3 = n_2 - n_1$ = number of electrons shared between atoms = number of bonding electrons.

$$\frac{n_3}{2} = \frac{n_2 - n_1}{2} = \text{number of shared (bonding) electron pairs} = \text{number of bonds.}$$

- (iv) Subtracting n_3 from n_1 gives n_4 .

$n_4 = n_1 - n_3$ = number of unshared electrons or non-bonding electrons

$$\frac{n_4}{2} = \frac{n_1 - n_3}{2} = \text{number of unshared electron pairs} = \text{number of lone pairs.}$$

- (v) Identify the central atom. Generally, the central atom is the one, which is least electronegative of all the atoms, when the other atoms do not contain hydrogen. When the other atoms are hydrogen only, then the central atom would be the more electronegative atom.
- (vi) Now around the central atom, place the other atoms and distribute the required number of bonds (as calculated in step (iv), keeping in mind that every atom gets an octet of electrons except hydrogen.
- (vii) Then calculate the formal charge on each atom of the species.

Formal charge is the difference between the valence electrons in an isolated atom and the number of electrons assigned to that atom in a Lewis Structure.

Formal charge on an atom = number of valence electrons of the atom – (number of shared electrons of that atom + number of unshared electrons of that atom).

Formal charge on an atom = number of valence electrons of the atom – number of bonds formed by that atom – number of unshared electrons (2 lone pairs) of that atom.

For every electron of an atom that is shared in a bond, the “number of bonds formed by the atom” is one. Therefore if an atom forms only one bond ($A - B$), one electron of the bond is that of A and other is that of B. So the “number of bonds” of A and B each is one. But if the bond were a co-ordinate bond ($A \rightarrow B$), then two electrons of A are involved in it. This makes the number of bonds of A to be 2 and that of B to be zero.

- (viii) When two adjacent atoms get opposite formal charges, then charges can be removed by replacing the covalent bond between the atoms by a dative (co-ordinate) bond. This bond will have the arrowhead pointing towards the atom with positive formal charge. It is not mandatory to show the dative bonds unless required to do so.
- (ix) The given Lewis structure should account for the factual aspects of the molecule like resonance (delocalization), bond length, $p\pi-d\pi$ back bonding etc.

Sometimes, there are more than one acceptable Lewis structure for a given species. In such cases, we select the most plausible Lewis structure by using formal charges and the following guidelines :

- For neutral molecules, a Lewis structure in which there are no formal charges is preferable to one in which formal charges are present.
- Lewis structures with large formal charges (+ 2, + 3 and/or – 2, – 3 and so on) are less plausible than those with small charges.
- Among Lewis structures having similar distributions of formal charges, the most plausible structure is the one in which negative formal charges are placed on the more electronegative atoms.

Example 1

Determine Lewis structure of NO_2^+ .**Solution :**

$$(i) \quad n_1 = 5 + (6 \times 2) - 1 = 16$$

$$(ii) \quad n_2 = (3 \times 8) = 24$$

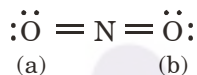
$$(iii) \quad n_3 = n_2 - n_1 = 24 - 16 = 8$$

$$\therefore \text{Number of bonds} = \frac{8}{2} = 4$$

$$(iv) \quad n_4 = n_1 - n_3 = 16 - 8 = 8$$

$$\therefore \text{Number of lone pairs} = \frac{8}{2} = 4$$

- (v) nitrogen is the central atom (as it is less electronegative than O). Arranging two O atoms around it and distributing 4 bonds and 4 lone pairs as



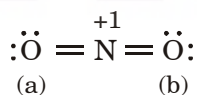
- (vi) Calculating formal charge on each atom.

$$\text{Formal charge on N} = 5 - 4 - 0 = +1$$

$$\text{Formal charge on O (a)} = 6 - 2 - 4 = 0$$

$$\text{Formal charge on O (b)} = 6 - 2 - 4 = 0$$

Thus, the structures can now be shown as



Example 2

Determine Lewis structure of CN^- ion.**Solution :**

$$(i) \quad n_1 = 4 + 5 + 1 = 10$$

$$(ii) \quad n_2 = (2 \times 8) = 16$$

$$(iii) \quad n_3 = n_2 - n_1 = 16 - 10 = 6$$

$$\therefore \text{Number of bonds} = \frac{6}{2} = 3$$

$$(iv) \quad n_4 = n_1 - n_3 = 10 - 6 = 4$$

$$\therefore \text{Number of lone pairs} = \frac{4}{2} = 2$$

(v) Carbon is the central atom (C is less electronegative than N) and arrange N, number of bonds and number of lone pairs around it as

$$(vi) \quad \text{Formal charge on C} = 4 - 3 - 2 = -1$$

$$\text{Formal charge on N} = 5 - 3 - 2 = 0$$

Thus, final Lewis structure of CN^- would be



Example 3

Draw Lewis structure for NH_4^+ ion.

Solution :

$$(i) \quad n_1 = 5 + (4 \times 1) - 1 = 8$$

$$(ii) \quad n_2 = (8 \times 1) + (2 \times 4) = 16$$

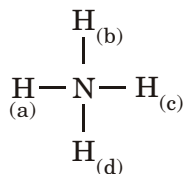
$$(iii) \quad n_3 = n_2 - n_1 = 16 - 8 = 8$$

$$\therefore \text{Number of bonds} = \frac{8}{2} = 4$$

$$(iv) \quad n_4 = n_1 - n_3 = 8 - 8 = 0$$

$$\therefore \text{Number of lone pairs} = 0$$

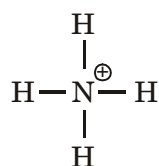
(v) Nitrogen being the central atom, distributing other atoms (H) around it, and 4 bonds with the 4 H atoms, the structure looks like



$$(vi) \quad \text{Formal charge on N} = 5 - 4 - 0 = +1$$

$$\text{Formal charge on H(a)/H(b)/H(c)/H(d)} = 1 - 1 - 0 = 0$$

Thus, final Lewis structure of NH_4^+ would be



6. COORDINATE BOND

It is a special type of covalent bond in which both the shared electrons are contributed by one atom only. It may be defined as “a covalent bond in which both electrons of the shared pair are contributed by one of the two atoms”. Such a bond is also called as dative bond. A coordinate or a dative bond is established between two such atoms, one of which has a complete octet and possesses a pair of valency electrons while the other is short of a pair of electrons.



This bond is represented by an arrow (\rightarrow).

The atom which contributes electron pair is called the donor while the atom which accepts it is called acceptor.

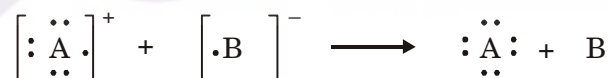
Note : Coordinate bond after formation is indistinguishable from a covalent bond.

The formation of a coordinate bond can be looked upon as a combination of electrovalent and covalent bonds. The formation may be assumed to have taken place in two steps:

- (i) The donor atom loses one electron and transferred to acceptor atom. As a result donor atom acquires a positive charge and the acceptor atom acquires a negative charge.



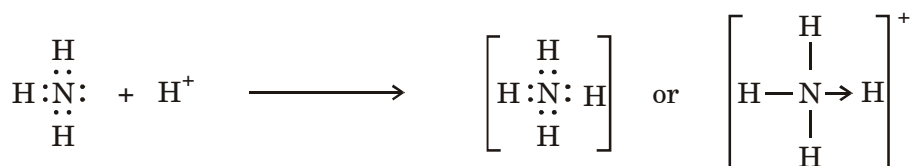
- (ii) These two charged particles now contribute one electron each and this pair is shared by both the atoms.



As the coordinate bond is a combination of one electrovalent bond and one covalent bond, it is also termed as semi polar bond.

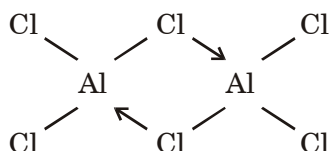
The compound consisting of the coordinate bond is termed coordinate compound. Some examples of coordinate bond formation are given below :

(1) Formation of ammonium ion : The ammonia molecule has a lone pair of electrons i.e. an unshared pair. The hydrogen ion H^+ , has empty s orbital. The lone pair comes to be shared between the nitrogen and hydrogen atoms.



Nitrogen atom is called the **donor** and H^+ , the **acceptor**. NH_3 is a neutral molecules. H^+ carries a unit positive charge, so NH_4^+ ion carries positive charge. Here, all the N–H bond become identical.

(2) **Formation of Aluminium Chloride, Al_2Cl_6**



(3) **Formation of ozone :** Oxygen molecule consists of two oxygen atoms linked by a double covalent bond. Each oxygen atom has two lone pairs of electrons. When one lone pair of electrons is donated to a third oxygen atom which has six electrons, a coordinate bond is formed.



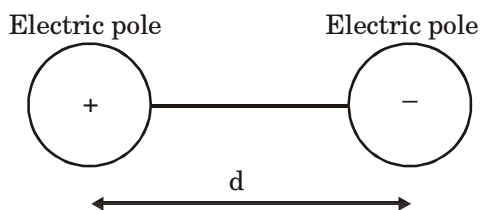
Characteristics of Coordinate Compounds

The properties of coordinate compounds are intermediate between the properties of electrovalent compounds and covalent compounds. The main properties are described below :

- (i) **Physical state :** These exist as gases, liquids and solids under ordinary conditions.
- (ii) **Melting and boiling points :** Their melting and boiling points are higher than purely covalent compounds and lower than purely ionic compounds.
- (iii) **Solubility :** these are sparingly soluble in polar solvents like water but readily soluble in non-polar (organic) solvents.
- (iv) **Stability :** These are as stable as the covalent compounds. The addition compounds are, however, not every stable. It is also a strong bond because the paired electrons cannot be separated easily.
- (v) **Conductivity :** Like covalent compounds, these are also bad conductors of electricity. The solutions or fused mass do not allow the passage of electricity.
- (vi) **Molecular reactions :** These undergo molecular reactions. The reactions are slow.
- (vii) **Isomerism :** The bond is rigid and directional. Thus, coordinate compounds show isomerism.
- (viii) **Dielectric constant :** The compounds containing coordinate bond possess high values of dielectric constants.

7. DIPOLE MOMENTS

A dipole consists of a positive and an equal negative charge separated by a distance within a molecule. The degree of polarity of a bond is given by the dipole moment (μ), which is the product of either charge (e) and the distance (d) between them. $\mu = de$. 'e' is of the order of magnitude of the electronic charge, i.e. about 10^{-10} esu and d is the distance between the atomic centres, i.e., about 10^{-8} cm. Hence dipole moment may be expected to have values around $10^{-10} \times 10^{-8} = 10^{-18}$ esu-cm. It is however, general practice to express dipole moments in **Debye units (D)**, $1 \text{ D} = 10^{-18}$ esu-cm.



If the charge is in SI units (Coulombs) and d in metre μ will coulomb-metre (C.m) units.

$$1\text{D} = 3.336 \times 10^{-30} \text{ C. m.}$$

Dipole moment is a **vector quantity**, i.e., it has both magnitude as well as direction. Thus the overall value of the dipole moment of a polar molecule depends on its geometry and shape i.e., vectorial addition of dipole moment of constituent bonds.

Any covalent bond which has a certain degree of polarity will have a corresponding dipole moment, though it does not follow that compounds containing such bonds will have dipole moments, for the polarity of the molecule as a whole is the vector sum of the individual bond moments. For example, CO_2 has zero dipole moment, although the $\text{C} = \text{O}$ bond is a polar bond. This shows that CO_2 is a linear molecule, $\text{O} = \text{C} = \text{O}$, so that the dipole moments of the two $\text{C} = \text{O}$ bonds cancel out. The $\text{C} \rightarrow \text{Cl}$ bond has a definite polarity and a definite dipole moment but carbon tetrachloride has zero dipole moment because it is a tetrahedral molecule, and the resultant of the $4\text{C} - \text{Cl}$ bond moments is zero. On the contrary CH_3Cl , CH_2Cl_2 and CHCl_3 have definite dipole moments.

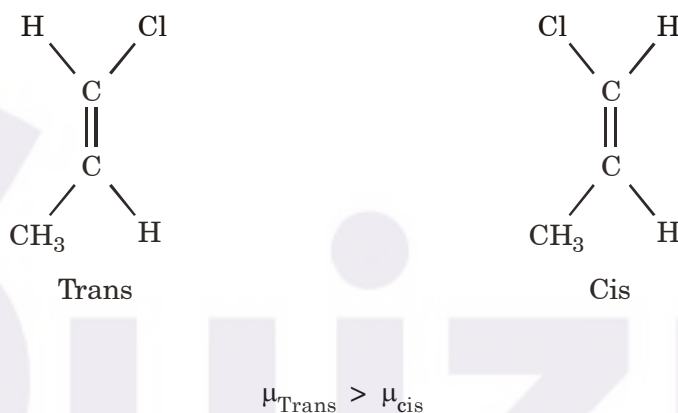
Applications of Dipole Moment

- (i) **To decide polarity of the molecule :** Molecules having zero dipole moment are said to be non-polar molecules and those having $\mu_R \neq 0$ are polar in nature.
- (ii) **To determine geometry of molecules :** The values of dipole moments provide valuable information about the structure of molecules.
 - (a) CO_2 , CS_2 molecules are linear as values of their dipole moments are zero.
 - (b) H_2O is not a linear molecule as it has dipole moment. Actually, it has V-shaped structure and the bond angle is 105° . Similarly, SO_2 has a bent structure.
 - (c) In ammonia, three hydrogen atoms do not lie symmetrically with respect to nitrogen as it has dipole moment. It has pyramidal structure.

- (iii) **To distinguish cis and trans forms of geometrical isomers :** Experimental values of dipole moment of the isomers (cis and trans) are determined. The trans isomer usually possesses either zero dipole moment or very low value in comparison to cis form.

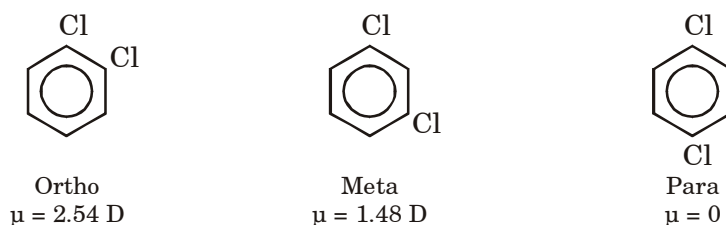


It should be noted that if two groups have opposite inductive character then trans isomer will have greater dipole moment of,



- (iv) **To determine orientation in benzene ring :** Dipole moment is useful to ascertain the orientation of substituents. The greater the dipole moment, the greater is the asymmetry. In general, dipole moment follows the order :

Ortho > meta > para

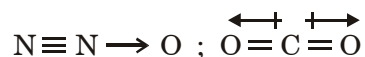


Example 4

Both CO_2 and N_2O are linear but dipole moment of CO_2 is zero but for N_2O it is non-zero, why ?

Solution :

The answer lies in the structure of these molecules. CO_2 is a symmetrical molecule while N_2O is unsymmetrical. Thus for N_2O , dipoles do not cancel each other, leaving the molecule with a resultant dipole moment, while the bond moment of CO_2 cancel each other, so CO_2 has no net dipole moment.

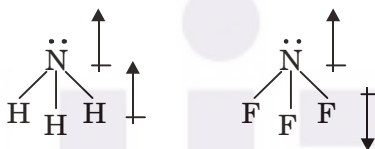


Example 5

Compare the dipole moment of NH_3 and NF_3 .

Solution :

Let's draw the structure of both the compounds and then analyse their dipole directions.



The structure of both NH_3 and NF_3 are pyramidal with three bond pairs and one lone pair. In NH_3 , as N is more electronegative than hydrogen, so the resultant bond dipole is towards N, which means that both the lone pair and bond pair dipoles are acting in the same direction and are summed up. In case of NF_3 , the bond dipole (of N-F bonds) is acting towards fluorine, (as fluorine is more electronegative than N) so in NF_3 the lone pair and bond pair dipoles are acting in opposition, resulting in a decreased dipole moment. Thus, NH_3 has higher dipole moment than NF_3 .

Dipole Moment and Percentage Ionic Character

The measured dipole moment of a substance may be used to calculate the percentage ionic character of a covalent bond in simple molecules.

$$1 \text{ unit charge} = \text{Magnitude of electronic charge} = 4.8 \times 10^{-10} \text{ e.s.u.}$$

$$1 \text{ D} = 1 \times 10^{-18} \text{ e.s.u.-cm}$$

$$\therefore \% \text{ ionic character} = \frac{\text{Observed dipole moment}}{\text{Theoretical dipole moment}}$$

Theoretical dipole moment is confined to when we assume that the bond is 100% ionic and it is broken into ions while observed dipole moment is with respect to fractional charges on the atoms of the bond.

Example 6

The dipole moment of LiH is 1.964×10^{-29} coulomb meter, distance between Li and H is 1.596 Å. Find the % ionic character in the molecule.

Solution :

$$\mu \text{ of } 100\% \text{ ionic molecule (Li}^+\text{H}^-) = 1.6 \times 10^{-19} \text{ C} \times 1.596 \times 10^{-10} \text{ m} = 2.554 \times 10^{-29} \text{ Cm}$$

$$\begin{aligned} \% \text{ ionic character} &= \frac{1.9 \times 10^{-29}}{2.554 \times 10^{-29}} \times 100 \\ &= 74.4\% \end{aligned}$$

Transition From Ionic to Covalent Bond–FAJANS' RULE

Just as a covalent bond may have partial ionic character an ionic bond may also show a certain degree of covalent character. When two oppositely charged ions approach each other closely, the cation would attract the electrons in the outer shell of the anion and simultaneously repel its nucleus. This produces distortion or polarisation of the anion, which is accompanied by some sharing of electrons between the ions, i.e., the bond acquires a certain covalent character.



The ability of a cation to polarise the near by anion is called its **polarising power** and the tendency of an anion to get distorted or deformed or polarised by the cation is called its **polarisability**.

Factors Influencing Ion – Deformation or Increasing Covalent Character

(i) Large charge on the ions :

The greater the charge on the cation, the more strongly will it attract the electrons of the anion. For example, Al^{3+} can distort Cl^- ion more than Na^+ ion. So aluminium chloride is a covalent compound whereas NaCl, AlF_3 , AgF are ionic.

(ii) Small cation and large anion :

For a small cation, the electrostatic force with which its nucleus will attract the anion will be large. Moreover a large anion cannot hold the electrons in its outermost shell, especially when they are attracted by a neighbouring cation. Hence there will be increased covalence with a small cation and a large anion, as in AgI.

(iii) Cation with a non-inert gas type of electronic configuration :

A cation with a 18 electron outermost shell such as Ag^+ ($[\text{Kr}] 4d^{10}$) polarizes anions more strongly than a cation with a 8 electron arrangements as in K^+ . The 'd' electrons in Ag^+ do not screen the nuclear charge as effectively as the 's' and 'p' electron shell in K^+ . Thus AgI is more covalent than KI, although Ag^+ and K^+ ions are nearly of the small size. Cuprous and mercurous salts are covalent.

The above statements regarding the factors which influence covalent character are called Fajans' rules. It can thus be seen easily that there is nothing like a purely ionic compound or a purely covalent compound.

8. SHAPES OF MOLECULES

The shapes or geometry of a molecule is quite accurately predicted by VSEPR (**valence shell electron-pair repulsion**) theory. According to this theory all valence shell electron pairs surrounding the central atom arrange themselves in such a manner as to be as far away from each other as possible. By separating the electrons from each other, electrostatic repulsion, (the cause of higher energy) is minimised. As a result each molecules tends to acquire a state of lowest energy.

The basic ideas can be summarized as follows :

Valence shell pairs of electrons are arranged about the central atom so that repulsions among them are minimized, or so that there is maximum separation among the regions of high electron density (bond pairs) about the atom. For instance, two regions of high electron density would be most stable on opposite sides of the central atom (the linear arrangement), while three regions would be most stable when they are arranged at the corners of an equilateral triangle (the trigonal planar arrangement). The resulting arrangement of these regions is referred to as the **electronic geometry** of the central atom.

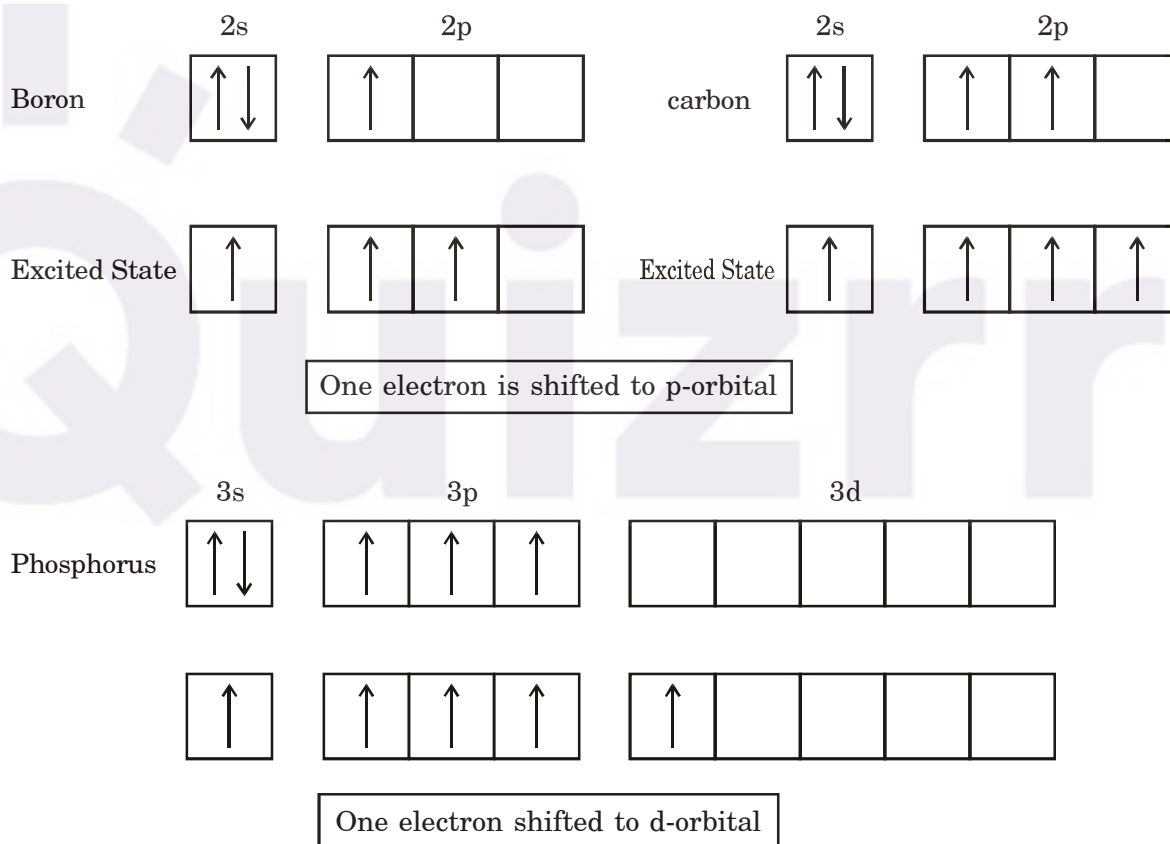
| Number of Region of High Electron Density (bp's) | Electronic Geometry | Bond Angles |
|--|----------------------|----------------|
| 2 | linear | 180 |
| 3 | trigonal planar | 120 |
| 4 | tetrahedral | 109 28 |
| 5 | trigonal bipyramidal | 90 , 120 , 180 |
| 6 | octahedral | 90 , 180 |

We will discuss this table detail a little later.

Some important points :

- (1) a covalent bond is formed by overlapping of atomic orbitals of valency shell of the two atoms. As a result of overlapping, there is maximum electron density somewhere between the two atoms.
- (2) Greater the overlapping, higher is the strength of chemical bond.
- (3) Electrons which are already paired in valency shell can enter into bond formation if they can be unpaired first and shifted to vacant orbitals of slightly higher energy of the same main energy shell. (Valency shell).

This point explains the trivalency of boron, tetravalency of carbon, pentavalency of phosphorus, hexavalency of sulphur in spite of the fact that these atoms have paired orbitals in the valency shell.



- (4) Between 2 orbitals of same stability (i.e. having same energy) one more directionally concentrated would form a stronger bond. Dumb-bell shaped p-orbitals will form a stronger bond as compared to spherically symmetrical s-orbital. It is formed by head on or axial overlap.

The types of bonds can be formed an account of overlapping.

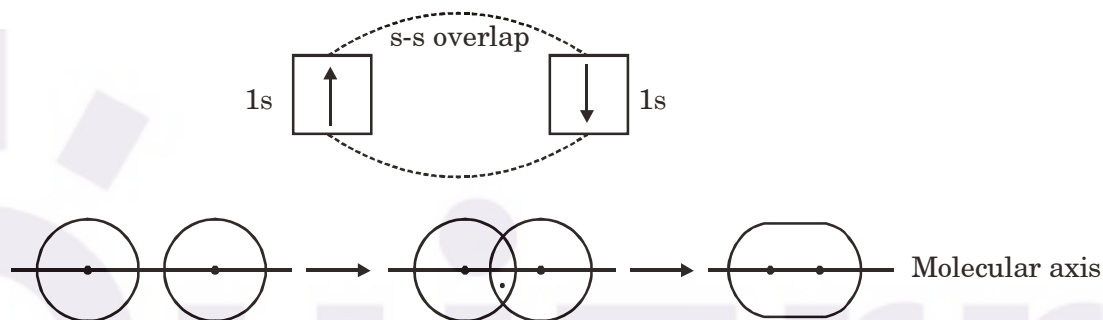
- (1) **Sigma Bond** : A bond formed between two atoms by the overlap of singly occupied orbitals along their axes (end to end overlap) is called sigma (σ) bond. The bond formed by this type of over lapping is very strong as the extent of overlapping is sufficiently high. In sigma bond, the electron density accumulates between the centres of the atoms being bounded and lies on the imaginary line joining the nuclei of bonded atoms.

Sigma bonds are formed by **three types** of overlapping.

- (i) **s-s overlapping** :

For example, **hydrogen molecule**.

Each hydrogen atom has one electron in is orbital which is spherical. Is orbital of both the hydrogen atoms approach each other closely and when they reach a point of maximum attraction by the two nuclei, they overlap and form a sigma bond.

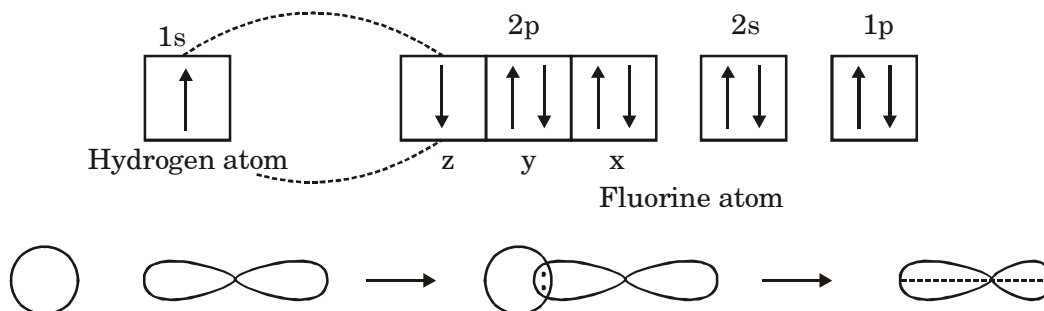


Formation of H_2 molecule by s-s overlapping

The bond has two electrons which have opposite spins. The probability of finding these electrons is maximum in the region between the two nuceli on the molecular axis. The electron density of the bond is distributed symmetrically about the molecular axis.

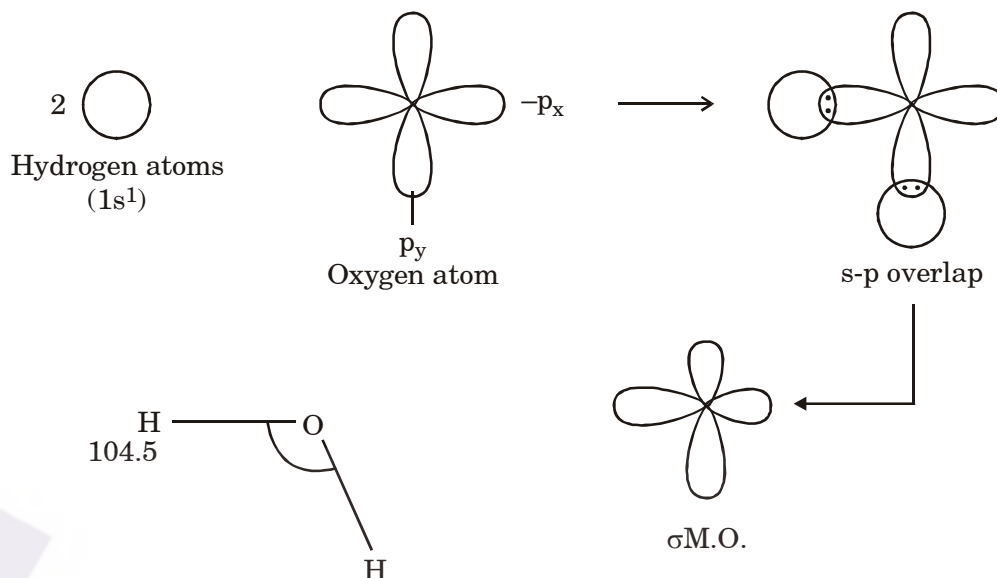
- (ii) **s-p overlapping (Formation of HF, H_2O molecules)** :

- (a) In the formation of HF molecule the 1s-orbital of hydrogen overlaps with the p-orbital of fluorine containing unpaired electron.



Formation of HF molecule by s-p overlapping

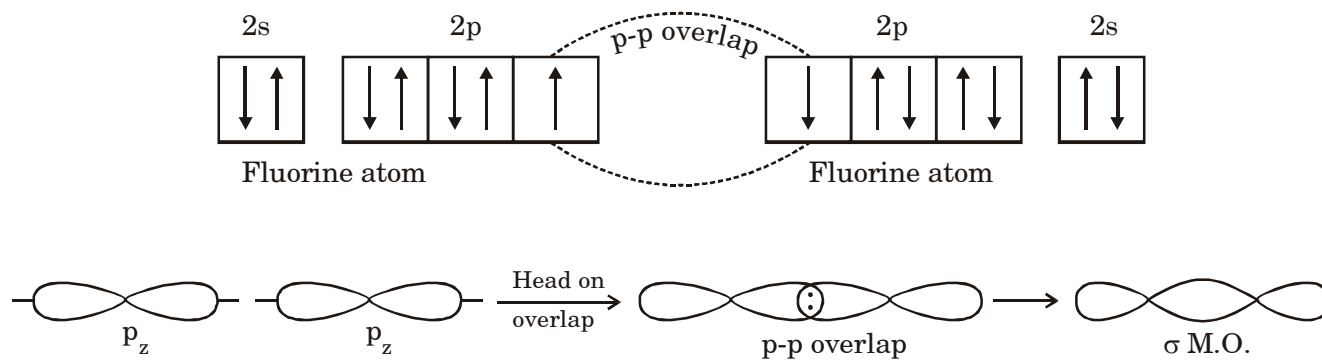
- (b) **Formation of water molecule :** Oxygen atom has the configuration of valency shell i.e., it has two orbitals singly occupied. These two orbitals overlap with 1 s-orbital of two hydrogen atoms forming sigma bonds.



Formation of water molecule by s-p overlapping

Since the two orbitals of oxygen are at right angle to each other an angle of 90° is expected between two sigma bonds but actual bond angle observed is 104.5° .

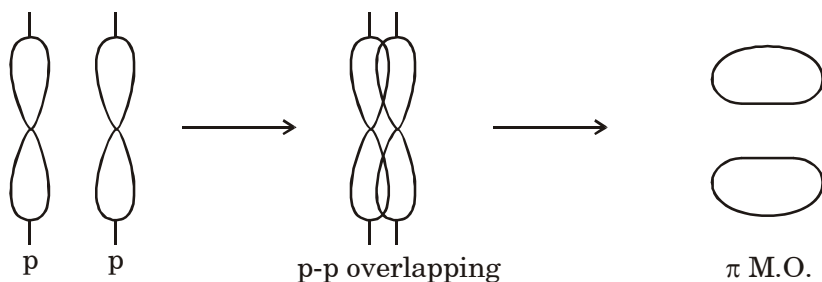
- (iii) **p-p overlapping (Formation of fluorine molecule) :** This is illustrated by the formation of fluorine molecule. The electronic configuration of fluorine atom is $1s^2 2s^2 2p_x^2 2p_y^2 2p_z^1$, i.e., one orbital is singly occupied. When p-orbitals of two fluorine atoms approach each other with their heads directly towards one another, they overlap and form a sigma bond.



Formation of F_2 molecule by p-p overlapping

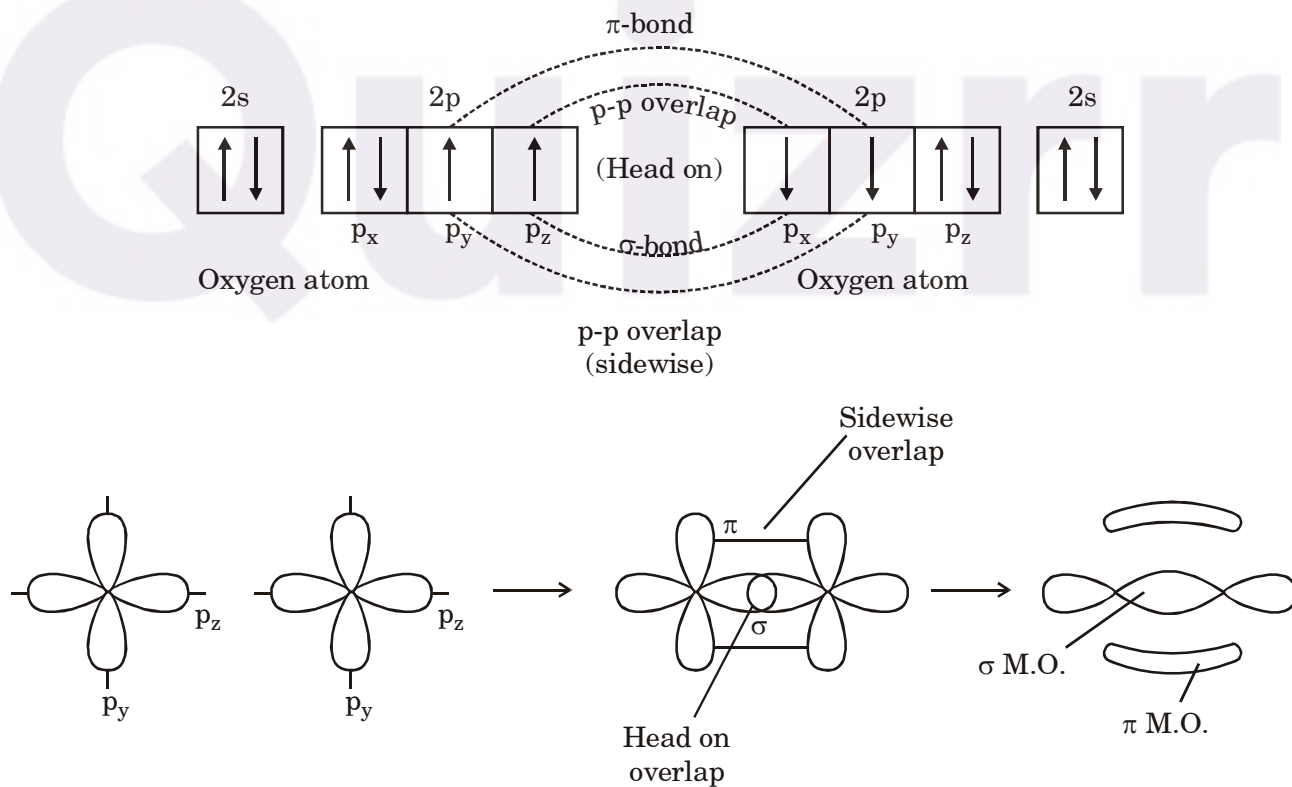
(2) Pi (π) Bond

π -bonds are formed by the sidewise or lateral overlapping of p-orbitals. The overlapping takes place at the side of two lobes and hence, the extent of overlapping is relatively smaller. Thus, π -bond is a weaker bond in comparison to sigma bond. The molecular orbital is oriented above and below the plane containing nuclear axis.



Formation of π -bond

Formation of oxygen molecule : Oxygen atom has two p-orbitals singly occupied in the valency shell. When two oxygen atoms approach each other, one set of p-orbitals experiences head on overlap forming a sigma bond while other set of p-orbitals overlaps sidewise to form a π -bond. Thus, oxygen molecule has one σ -and one π -bond.



Formation of O_2 molecule

Similarly, the formation of nitrogen molecule can be explained. It has one sigma bond and two π -bonds.

All single bonds are sigma bonds. A double bond consists of one sigma and one π -one while a triple bond consists of one sigma and two π -bonds.

- (i) **Bond energy** increases from a single bond to a trip bond.

Bond energy : Single bond < Double bond < Triple bond

- (ii) **Bond strength** increases from a single bond to a triple bond.

Bond strength : Single bond < Double bond < Triple bond

- (iii) **Bond length** of a multiple bond (double or triple) is always shorter than the corresponding single bond.

Bond length : Single bond > Double bond > Triple bond

- (iv) **Reactivity** of a multiple bond is always more than the single bond. This is due to the fact that π -electrons are mobile in nature.

Reactivity : Single bond < Double bond < Triple bond.

9. HYBRIDIZATION

The valence bond theory (overlapping concept) explains satisfactorily the formation of various molecules but it fails to account the geometry and shapes of various molecules. It does not give explanation why BeCl_2 is linear, BF_3 is planar. CH_4 is tetrahedral, NH_3 is pyramidal and water is V-shaped molecule. In order to explain these cases, the valence bond theory has been supplemented by the concept of hybridization. This is a hypothetical concept and has been introduced by Pauling and Slater. According to this concept any number of atomic orbitals of an atom which differ in energy slightly may mix with each other to form new orbitals called hybrid orbitals. The process of mixing or amalgamation of atomic orbitals of nearly same energy to produce a set of entirely new orbitals of equivalent energy is known as hybridization. The following are the rules of hybridization :

- Only orbitals (atomic) of nearly same energy belonging to same atom or ion can take part in hybridization.
- Number of the hybrid orbitals formed is always equal to number of atomic orbitals which have taken part in the process of hybridization.
- Most of the hybrid orbitals are similar but they are not necessarily identical in shape. They may differ from one another in orientation in space.
- Actually the orbitals which undergo hybridization and not the electrons. For example, for orbitals of nitrogen atom ($2s^2 2p_x^1 2p_y^1 2p_z^1$) belonging to valency shell when hybridize, form four hybrid orbitals, one of which has two electrons (as before) and other three have one electron each.

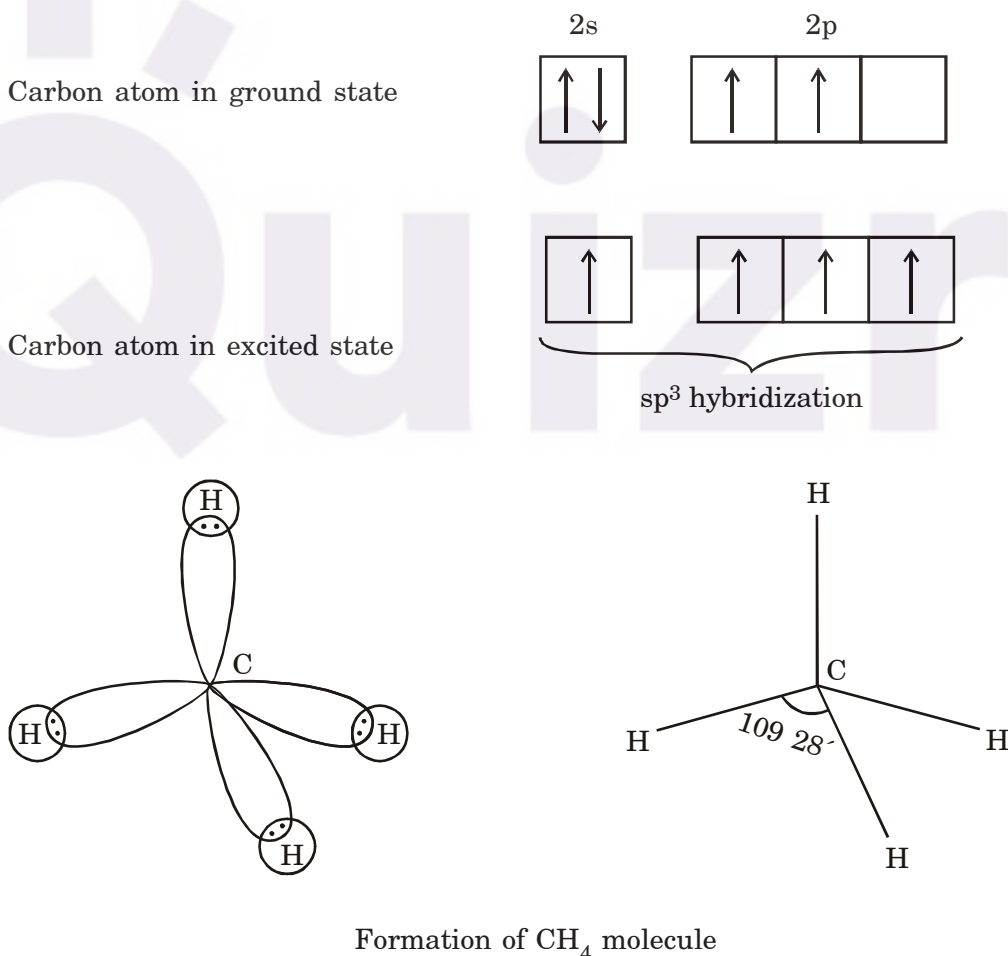
- (v) Hybrid orbitals only form sigma bonds.

It is concept not only predicts the correct shapes but also explains the actual microscopic observations of the geometry of molecules. The different cases of hybridisation arises by mixing of s,p,d orbitals; few of them are discussed below.

Sp^3 Hybridisation

This type of hybridisation results from mixing of one s, three p orbitals of outer (valence) shell of an atom. Let us take the example of CH_4 molecule.

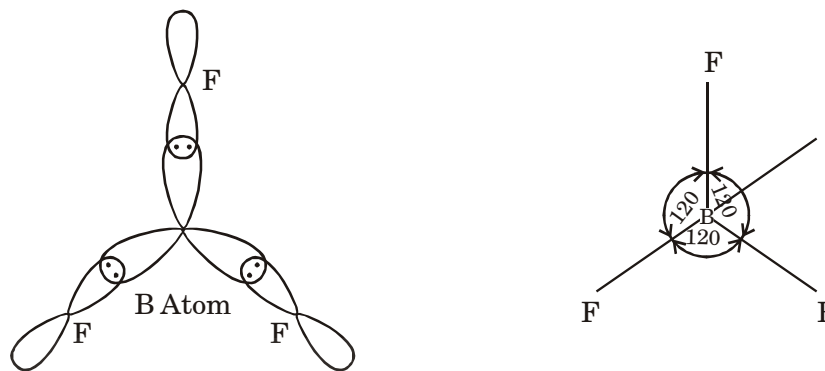
Carbon atom has configuration $1s^2, 2s^2 2p_x^1 2p_y^1$. In ground state, it has two unpaired orbitals which can form only two covalent bonds. To get tetravalency, 2s-orbital is unpaired and the electron is shifted to 2p-orbital. Now in excited state the four unpaired orbitals undergo hybridization giving rise to four hybrid orbitals which are $109^\circ 28'$ apart. The four hybrid orbitals overlap with s-orbital of each of the four hydrogen atoms forming four sigma bonds. The molecule formed is tetrahedral.



Sp² Hybridisation

To understand it let us take the example of BF₃ molecule.

BF₃ molecule : Boron atom has configuration 1s², 2s² 2p¹. In ground state, it has one unpaired orbital which can form only one covalent bond. To get trivalency, the 2s-orbital is unpaired and the electron is shifted to 2p-orbital. Now in excited state the three unpaired orbitals undergo

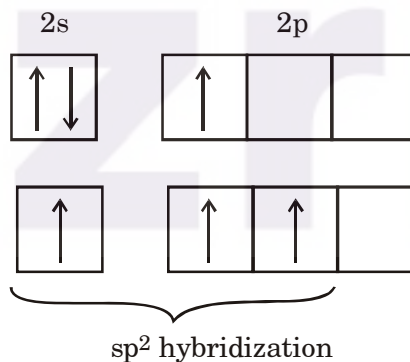


Formation of BF₃ molecule

hybridization giving rise to three hybrid orbitals which are 120° apart. The three hybrid orbitals overlap with three p-orbitals from three fluorine atoms forming three sigma bonds. The molecule formed is triangular and planar.

Boron atom in ground state 1s², 2s² 2p_x¹

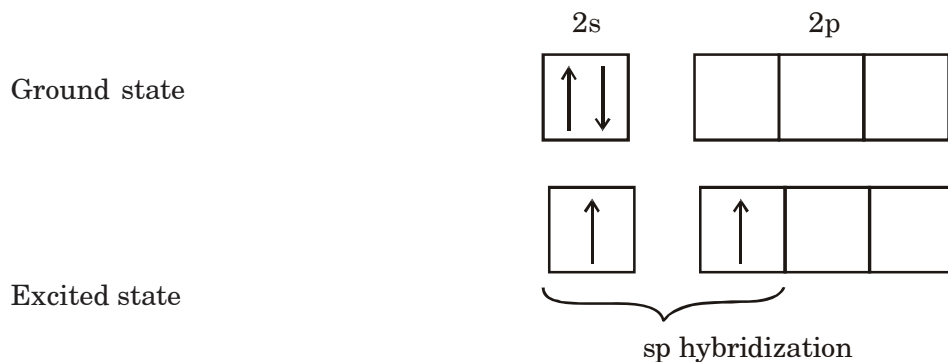
Boron atom in excited state 1s², 2s¹ 2p_x¹ 2p_y¹



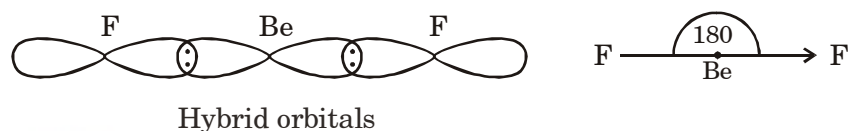
Sp Hybridisation

An sp hybrid orbital is formed when in an atom one s and one p orbital mix with each other to form two equivalent orbitals. Two such orbitals i.e. sp hybrid orbitals are most stable when they adopt an angle of 180° between them so that they are at the maximum distance apart. Hence, the shape is linear.

BeF₂ molecule explains sp hybridisation Beryllium atom has the configuration 1s², 2s². Since there are no unpaired electrons in the valence shell, it cannot form any covalent bond. Thus, 2s-orbital is first unpaired and an electron is shifted to 2p-orbital.



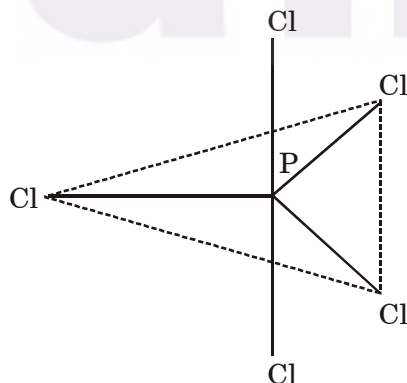
These s and p orbitals overlap with p-orbital of fluorine atoms forming two sigma bonds. The molecule formed is linear with a bond angle 180° .



Formation of BeF_2 molecule

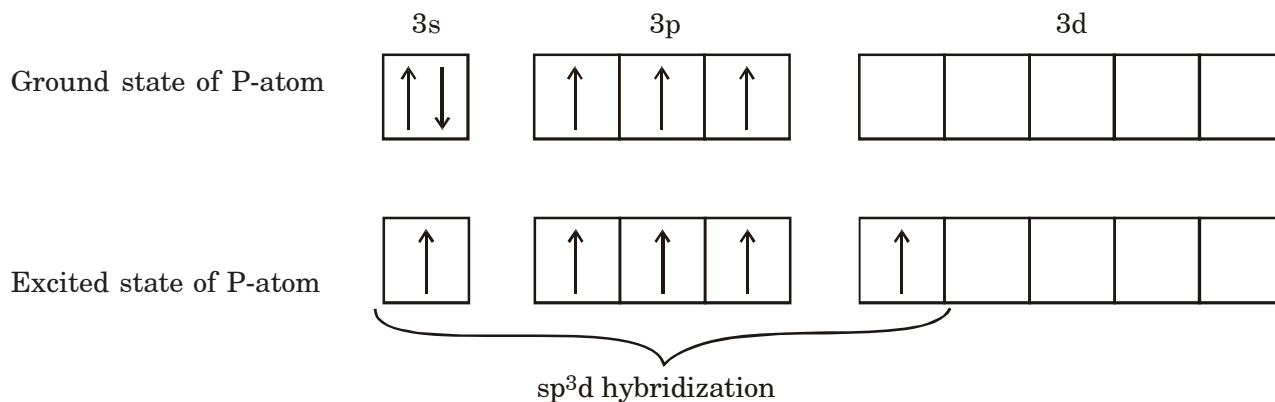
Sp^3d hybridisation

PCl_5 molecule : P-atom has configuration $1s^2, 2s^2, 2p^6, 3s^2, 3p_x^1, 3p_y^1$. In ground state, it can form three covalent bonds as three unpaired orbitals are present in the valency shell. To get pentavalency, 3s-orbital is unpaired and the electron is shifted to 3d-orbital. Now in the excited state the five orbitals involving one s-, one d- and three p-orbitals



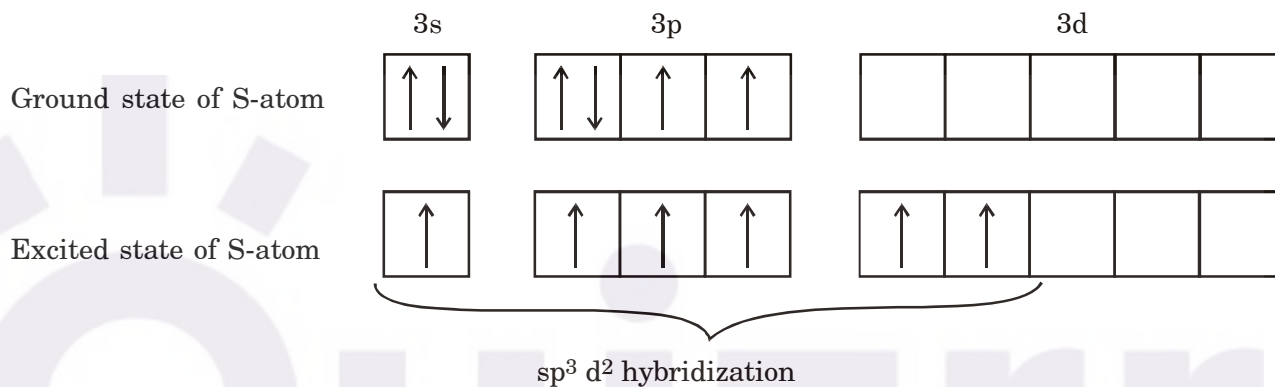
Trigonal bipyramid

undergo hybridization giving birth to five hybrid orbitals which overlap with five chlorine atoms forming five sigma bonds. Out of five σ -bonds, three bonds which are located at 120° angle are equatorial and the remaining two are axial. Axial bond length is greater.

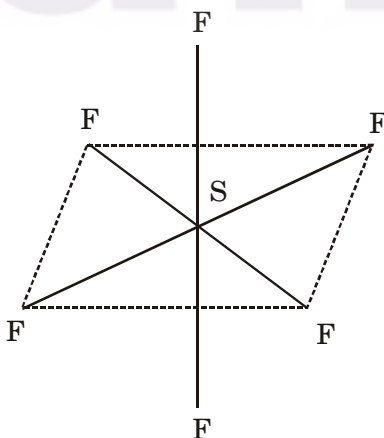


Sp^3d^2 Hybridisation

SF₆ Molecule :



3s-and paired 3p-orbital are unpaired and electrons are shifted to d-orbitals. After hybridization six hybrid orbitals directed towards the corners of a regular octahedron come into existence which overlap with six fluorine atoms. The SF₆ molecule has octahedral structure.

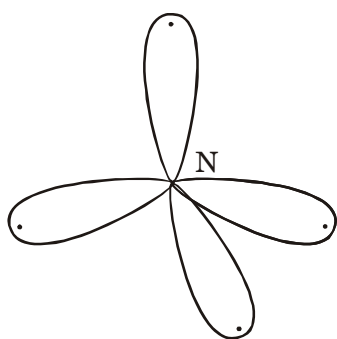


Note : Please note that sp^3d and sp^3d^2 hybridisation cannot be shown by elements of 2nd period (e.g. Nitrogen, oxygen, Fluorine etc.) because of the absence of low-energy d-orbitals available for hybridisation.

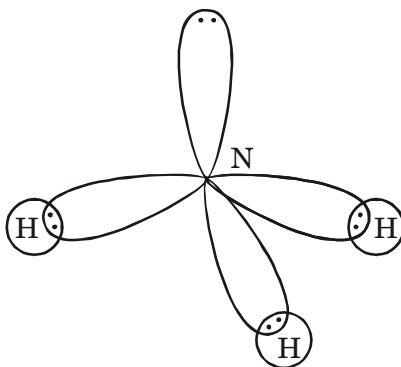
Hybridisation and Geometry of some molecules Containing lone pairs of Electrons

Sp³ Hybridisation

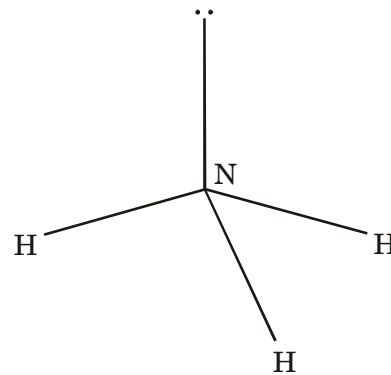
(a) **NH₃ molecule** : Nitrogen atom undergoes sp³ hybridization forming four hybrid orbitals.



Hybrid orbitals of N

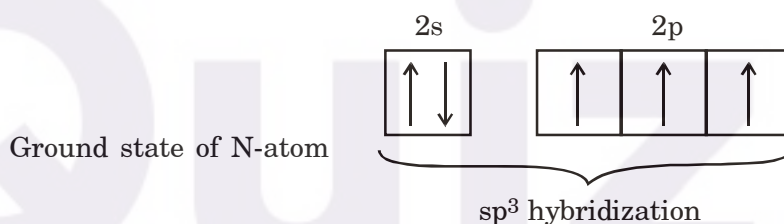


Overlapping with hydrogen atoms



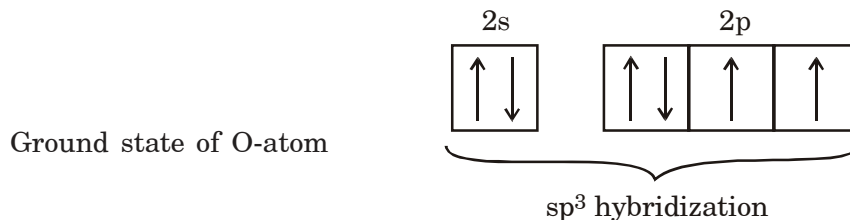
Ammonia

Three of the hybrid orbitals contain one electron each while the fourth one has a pair of electrons. Three hybrid orbitals having one electron each overlap with three hydrogen atoms forming three sigma bonds while the lone pair of fourth hybrid orbitals remains unused.

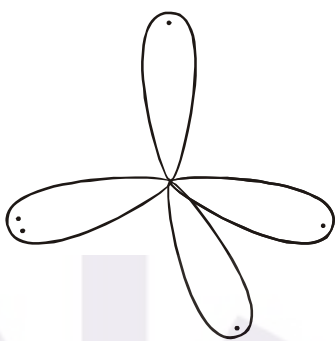


The expected bond angle should be 109° 28' but the actual bond angle is 106° 45' because of the repulsion between lone pair and bonded pairs due to which contraction occurs. Thus, ammonia molecule is pyramidal in shape.

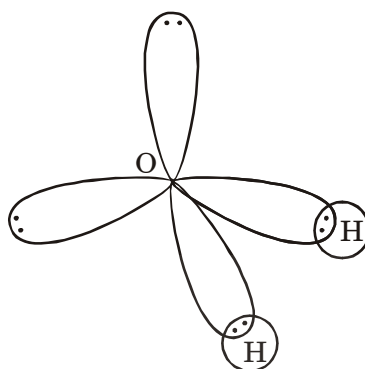
(b) **H₂O molecule** : Oxygen atom undergoes sp³ hybridization forming four hybrid orbitals. Two of the hybrid orbitals contain one electron each while other two a pair of electrons each. The hybrid orbitals having one electron each overlap with hydrogen atoms forming two sigma bonds while the lone pairs of the other hybrid orbitals remain unused.



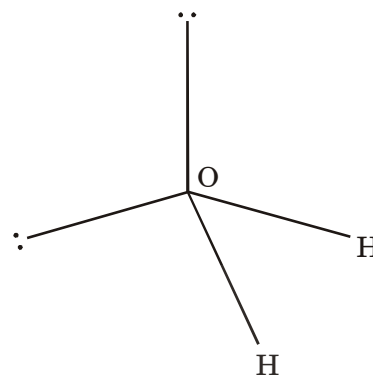
The expected bond angle is $109^{\circ} 28'$ but the actual bond angle is $104^{\circ} 35'$. This is due to the presence of two lone pairs which repel each other and the bonded pairs more strongly and cause them to come closer and thereby reducing the bond angle from $109^{\circ} 28'$ to $104^{\circ} 35'$. Similarly, the geometry of PH_3 , PCl_3 , NF_3 , H_2S , etc., can be explained. It is clear from the above two structures that higher the number of lone pairs present on a central atom, the greater is the contraction caused in the bond angle. The bond angle is also decreased as the size of the central atom increases. The bond angle in PH_3 is $93^{\circ} 20'$.



Hybrid orbitals of O



Overlapping with hydrogen atoms

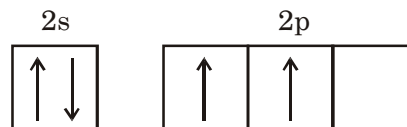


Water molecule (V-shaped)

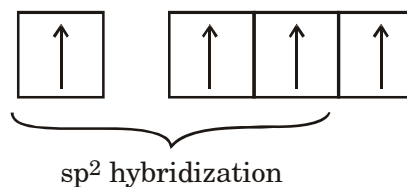
Geometry and hybridisation of Molecules having multiple bonds

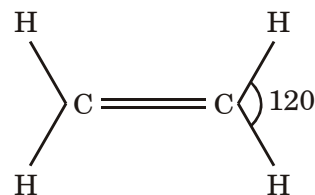
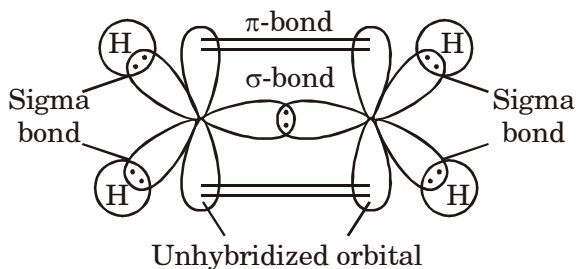
- (i) **Ethylene molecule (C_2H_4)** : Ethylene molecule is formed as a result of sp^2 hybridization of carbon. Each carbon atom in excited state undergo sp^2 hybridization giving rise to three hybrid orbitals each. These hybrid orbitals lie in the xy plane while the fourth unhybridized orbital lies at right angle to the hybridized orbitals. In the formation of ethylene two hybrid orbitals, i.e., one from each carbon atom form a sigma bond by head on overlap while the remaining overlap with hydrogen atoms. The unhybridized p-orbitals undergo sideways overlap to form a π -bond.

Ground state of carbon atom



Excited state of carbon atom

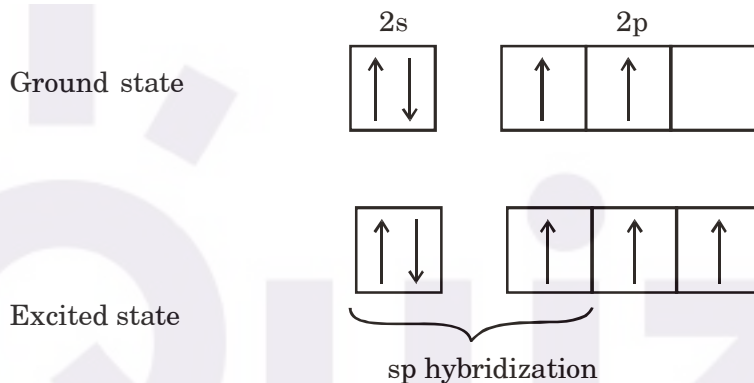




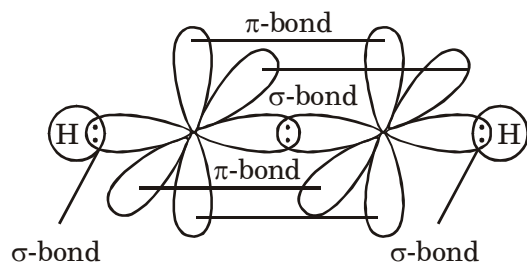
Formation of Ethylene molecule

Acetylene molecule (C_2H_2) :

It is formed as a result of sp hybridisation of carbon. Each carbon atom in excited state undergoes sp hybridisation giving rise to two hybrid orbitals each. Each carbon atom is left with two unhybridized p -orbitals.



The two hybrid orbitals of each carbon atom are used up in forming $\text{C} - \text{C}$ and $\text{C} - \text{H}$ sigma bonds. The unhybridized orbitals overlap sidewise to form two π -bonds.



Acetylene is linear structure.

10. VSEPR THEORY

As already explained, VSEPR theory says that "all valence shell electron pairs surrounding the central atom arrange themselves in such a manner as to be as far away from each other as possible".

possible". Thus, the mutual interaction among the electrons orient the orbitals in space to an equilibrium position where repulsion becomes minimum. The extent of repulsive interaction then follows the order **lone pair-lone pair > lone pair bond pair > bond pair-bond pair**.

Example 7

Why the bond angle of H — C — H in methane (CH_4) is $109^\circ 28'$ while H — N — H bond angle in NH_3 is 107° though both carbon and nitrogen are sp^3 hybridized ?

Solution :

In CH_4 , there are 4 lone pair of electrons while in NH_3 are 3 bond pair of electrons and 1 lone pair of electrons since bond pair-bond pair repulsion is less than lone pair-bond pair repulsion, in NH_3 bond angle is reduced of $109^\circ 20'$ to 107° .

Example 8

The bond angle of H_2O is 104° while that of F_2O is 102° . Why ?

Solution :

Concept : "If the electronegativity of the peripheral atoms is more, then the bond angle will be less".

Here, both F_2O and H_2O have a lone pair of electrons. But Fluorine is highly electronegative thus electrons are drawn more towards F in F_2O , whereas in H_2O it is drawn towards O. So there will be more repulsion in H_2O molecule between the adjacent bond pairs. Hence the bond angle will be more.



Example 9

Out of H_2O and H_2S which is having greater bond angle and why ?

Solution :

Concept : "If the electronegativity of central atom is more, then bond angle will be more"

Here since Oxygen is more electronegative than sulphur, hence oxygen draws the shared pair more towards itself. Hence bond pair repulsion is more in case of H_2O .

PREDICTION OF SHAPE OF COVALENT MOLECULES

Geometry can be easily predicted if the state of hybridization of the central atom is known. Steps for knowing the state of hybridization of central atom.

- (1) Detect the central atom
- (2) Count the number of σ -bonds
- (3) Count the number of lone pair of electrons on central atom.
- (4) Adding the two, if total is 4, the hybridization is sp^3 . If this total is 3, the hybridization is sp^2 and if total is 2, hybridization is sp .

Note : This is a shortcut method and is not applicable to all molecules.

Some Examples :

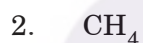
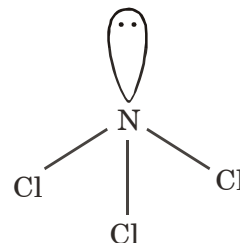


σ bonds = 3

lone pair on N = 1

hybridization = sp^3

shape = pyramidal

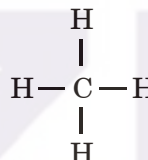


σ -bonds = 4

lone pair on C = 0

hybridization = sp^3

shape = Tetrahedral

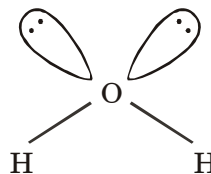


σ -bonds = 2

lone pair on O = 2

Hybridization = sp^2

shape = V-shape (bent)

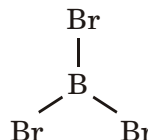


σ bond = 3

lone pair = 0

hybridization = sp^2

shape = trigonal planar

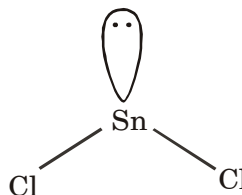


5. SnCl_2 σ -bonds = 2

lone pair = 1

hybridization = sp^2

shape = bent

6. BeCl_2 σ -bonds = 2

lone pair = 0

hybridization = sp

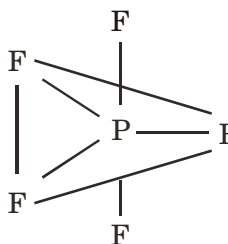
shape = linear

7. PCl_5 σ -bonds = 5

lone pair = 0

hybridization = sp^3d

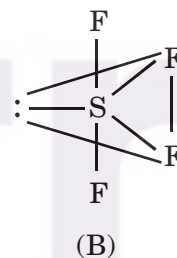
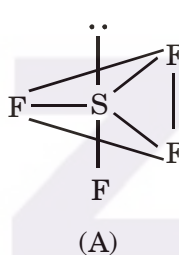
shape = Trigonal bipyramidal

8. SF_6 σ -bonds = 6

lone pair = 0

hybridization = sp^3d

shape = Trigonal bipyramidal



Since it is trigonal bipyramidal structure hence, 2 structures are possible.

Here, the lone pair is placed at different positions. In [B], it is at equatorial position and in [A], it is at axial position.

Now, when a lone pair is at equatorial position, the repulsion is minimized.

So structure [B] is correct :

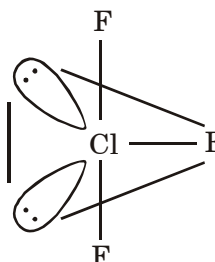
Note : Whenever there are lone pairs in TBP geometry, they should be placed in equatorial position so that repulsion is minimum.

9. ClF_3 σ -bonds = 3

lone pair = 2

hybridization = sp^3d

shape = T-shaped.



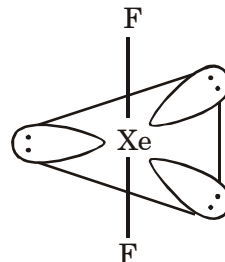
Please note that the lone pairs are placed at equatorial position for repulsion to be minimized. Now, students may be wondering that the hybridization is sp^3d so shape should be TBP. But if we see only the bonds, it gives us the impression of T-shape.

10. XeF_2 σ -bonds = 2

lone pair = 3

hybridization = sp^3d

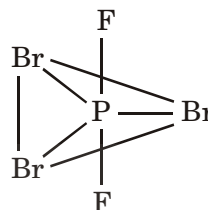
shape = linear

11. PF_2Br_3 σ -bonds = 5

lone pair = 0

hybridization = sp^3d

shape = Trigonal bipyramidal



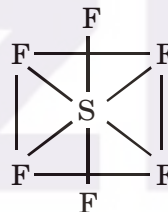
Here we see that fluorine is placed in axial position whereas bromine is placed in equatorial position. This is because, fluorine being more electronegative pulls away bonded electron towards itself more than it is done by bromine atom which results in decrease in bond pair-bond pair repulsion and hence, it is placed in axial position.

12. SF_6 σ -bonds = 6

lone pairs = 0

hybridization = sp^3d^2

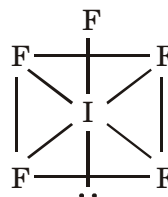
shape = octahedral/square bipyramidal

13. IF_5 σ -bonds = 5

lone pair = 1

hybridization = sp^3d^2

shape = square pyramidal

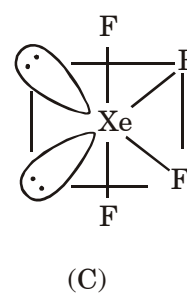
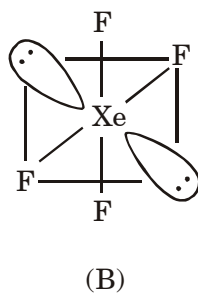
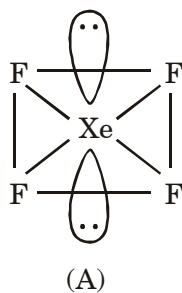
14. XeF_4 σ -bonds = 4

lone pairs = 2

hybridization = sp^3d^2

shape = square planar

Here 3 structures are possible.



Now [A] and [B] are same, they can be inter converted by simple rotation of molecule. The basic difference between [B] and [C] is that in [B] the lone pair is present in the anti-positions which minimize the repulsion which is not possible in structure [C] where the lone pairs are adjacent. So, in an octahedral structure, the lone pairs must be placed at the axial positions to minimize repulsion. So both structure [A] and [B] are correct.

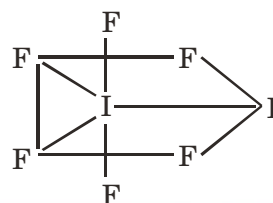
15. IF_7

σ -bonds = 7

lone pair = 0

hybridization = sp^3d^3

shape = pentagonal bipyramidal



Alternate Method

Now, it becomes very difficult if the compound is unknown and students do not know the number of π -bonds and σ -bonds. Also, in cases of ionic compounds, calculating the hybridization and shape is difficult. Hence, to solve such problems we can apply another method which will be applicable everywhere.

Steps to be employed :

- (1) Identify the central atom along with peripheral atoms.
- (2) Count the total valence electrons of the Central and peripheral atoms.
- (3) Add the electrons in case of anionic species and subtract the electrons in case of cationic species.
- (4) If the above value is less than or equal to 8, divide it by 2 and if the value is greater than 8, divide it by 8.
- (5) The quotient plus (remainder/2) gives us the total number of hybrid orbitals.

Some examples

1. HCN

Total valence electrons = $1 + 4 + 5 = 10$

Divide by 8

so, $N = 1 + 1$

Hence, hybridization = sp

shape = linear



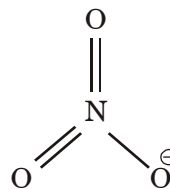
2. NO_3^-

Total valence electrons = $5 + 3 \times 6 + 1 = 24$

So, $N = 3 + 0$

hence, hybridization = sp^2

shape = Trigonal planar



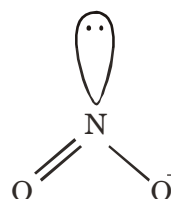
3. NO_2^-

Total valence electrons = $5 + 2 \times 6 + 1 = 18$

So, $N = 2 + 1$

hence, hybridization = sp^2

shape = angular / bent



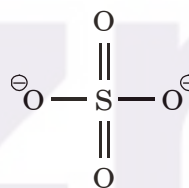
4. SO_4^{2-}

Total valence electrons = $6 + 4 \times 6 + 2 = 32$

So, $N = 4 + 0$

hybridization = sp^3

shape = Tetrahedral



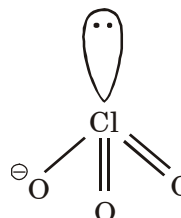
5. ClO_3^-

Total valence electrons = $7 + 3 \times 6 + 1 = 26$

So, $N = 3 + 1$

hybridization = sp^3

shape = trigonal pyramidal



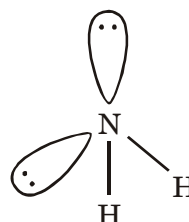
6. NH_2^-

Total valence electrons = $5 + 2 \times 1 + 1 = 8$

So, $N = 4 + 0$

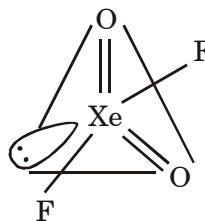
hybridization = sp^3

shape = bent

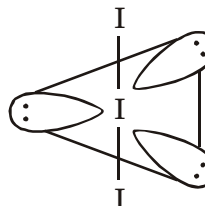


7. XeO_2F_2 Total valence electrons = $8 + 6 \times 2 + 7 \times 2 = 34$ So, $N = 4 + 1$ hybridization = sp^3d

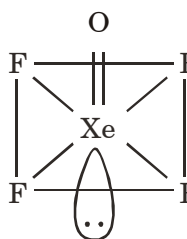
shape = distorted TBP (sea – saw geometry)

8. I_3^- Total valence electrons = $3 \times 7 + 1 = 22$ So, $N = 2 + 3$ hybridization = sp^3d

shape = linear

9. XeOF_4 Total valence electrons = $8 + 6 + 4 \times 7 = 42$ So, $N = 5 + 1$ hybridization = sp^3d^2

shape = square pyradinal



Molecular Shapes

| No. of electron pairs over central atom | Type of hybridisation | Geometry of molecules as per VSEPR theory | No. of bonded atoms | No. of lone pairs | Actual shape of molecules | Examples |
|---|-----------------------|---|---------------------|-------------------|---------------------------|--|
| 2 | sp | Linear, 180 | 2 | 0 | Linear | CO_2 , HgCl_2 , BeF_2 , ZnCl_2 , MgCl_2 , C_2H_2 , HCN |
| 3 | sp^2 | 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 |
| | | < 120 | 2 | 1 | V-shape (bent) | NO_2^- , SO_2 , SnCl_2 |
| 4 | sp^3 | Tetrahedral, 109.5 | 4 | 0 | Tetrahedral | CH_4 , SiH_4 , SO_4^{2-} , SnCl_4 , ClO_4^- , BF_4^- , NH_4^+ |
| | | < 109.5 | 3 | 1 | Trigonal pyramid | NH_3 , PCl_3 , PH_3 , AsH_3 , ClO_3^- |
| | | 104.5 | 2 | 2 | V-shaped (bent) | H_2O , H_2S , PbCl_2 , OF_2 , NH_2^- , ClO_2^- |
| 5 | sp^3d | Trigonal bipyramid | 5 | 0 | Trigonal pyramid | PCl_5 , SbCl_5 |
| | | | 4 | 1 | | TeCl_4 , SF_4 |
| | | | 3 | 2 | T-shaped | ClF_3 , IF_3 |
| | | | 2 | 3 | Linear | I_3^- , XeF_2 |

| No. of electron pairs over central atom | Type of hybridisation | Geometry of molecules as per VSEPR theory | No. of bonded atoms | No. of lone pairs | Actual shape of molecules | Examples |
|---|-----------------------|---|---------------------|-------------------|---------------------------|----------------------------------|
| 6 | sp^3d^2 | Octahedral | 6 | 0 | Octahedral | SF_6 , PF_6^- , $SnCl_6^-$, |
| | | | 5 | 1 | Square pyramidal | ICl_5 , BrF_5 , IF_5 |
| | | | 4 | 2 | square planar | XeF_4 , ICl_4^- |
| 7 | s^3d^3 | Pentagonal bipyramid | 7 | 0 | Pentagonal bipyramid | IF_7 |
| | | | 6 | 1 | distorted octahedral | XeF_6 |

Example 4

Considering x-axis as the internuclear axis, which out of the following will form a sigma bond ?

- (a) 1s and 1s
- (b) 1s and $2p_x$
- (c) $2p_y$ and $2p_y$
- (d) $2p_x$ and $2p_y$
- (e) 1s and 2s

Solution :

The sigma bond is formed by axial overlap and is present in the following cases :

- (a) 1s and 1s
- (b) 1s and $2p_x$
- (c) 1s and 2s

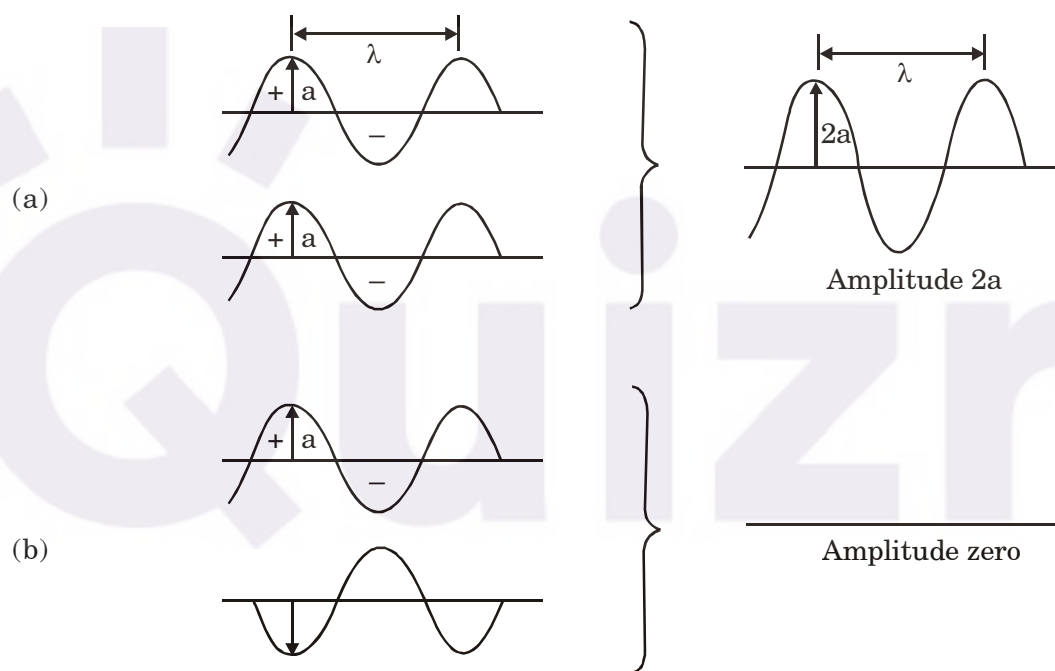
11. MOLECULAR ORBITAL THEORY

The valence bond theory is based on the assumption that the formation of a molecule involves an interaction between the electron waves of only those atomic orbitals of the participating atoms which are half filled. These atomic orbitals mix with one another to form a new orbital of greater stability while all other orbitals on the atoms remain undisturbed or maintain their individual identity. But this cannot be correct because the nucleus of one approaching atom is bound to affect the electron waves of nearly all the orbitals of the other atom. Besides this in valence bond theory fails to explain the formation of coordinate bond, the paramagnetic character of O_2 molecule and the formation of odd electron molecules or ions such as H_2^+ ion where no pairing of electron occurs.

Molecular orbital theory of chemical bonding is more rational and more useful in comparison to valence bond theory. This theory was put forward by Hund and Mulliken. According to this

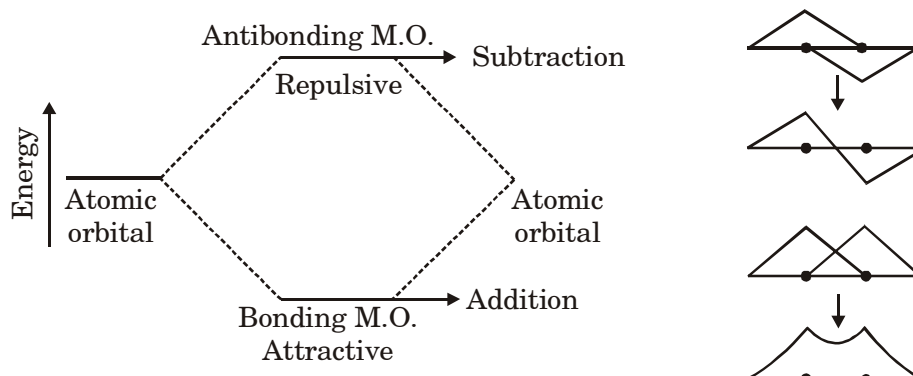
theory, all the atomic orbitals of the atoms participating in molecule formation get disturbed when the concerned nuclei approach nearer. They all get mixed up to give rise to an equivalent number of new orbitals that belong to the molecule now. These are called molecular orbitals. The electrons belonging originally to the participating atoms are now considered to be moving along the molecular orbitals under the influence of all the nuclei.

Linear combination of atomic orbitals (LCAO); Formation of bonding and antibonding molecular orbitals : Molecular orbitals of a molecule are obtained by the linear combination of atomic orbitals of the bonded atoms. The electron waves that describe the atomic orbitals have positive and negative phase or amplitude just as there are positive (upward) and negative (downward) amplitudes associated with standing wave. When wave are combined, they may interact either constructively or destructively. If the two identical waves are added, they combine constructively to produce the wave with double the amplitude and same wavelength. Conversely, if they are subtracted, they combine destructively to produce the wave with zero amplitude.



Likewise when two atomic orbitals overlap they can be in phase (added) or out of phase (subtracted). If they overlap in phase, constructive interaction occurs in the region between two nuclei and a bonding orbital is produced. The energy of the bonding orbital is always lower (more stable) than the energies of the combining atomic orbitals. When they overlap out of phase, destructive interference reduces the probability of finding an electron in the region between the nuclei and antibonding orbital is produced. The energy of an antibonding orbital is higher (less stable) than the energies of the combining atomic orbitals. The antibonding orbitals are represented by subscript asterisks, i.e., σ^* , π^* , δ^* , etc. Thus, the number of molecular orbitals formed from atomic orbitals

is equal to the number of atomic orbitals responsible for their formation. The formation can be represented graphically.



The different notations for representing bonding and anti-bonding Molecular orbitals are

| Atomic orbitals that are mixed | s and s | P_z and P_z | P_x and P_x | P_y and P_y |
|--------------------------------|------------|-----------------|-----------------|-----------------|
| Bonding M.O. | σs | $\sigma(p_z)$ | $\pi(p_x)$ | $\pi(p_y)$ |
| Antibonding M.O. | σs | $\sigma^*(p_z)$ | $\pi^*(p_x)$ | $\pi^*(p_y)$ |

We have assumed the two p_z orbitals to overlap end to end, so that the M.O. formed is of the ' σ ' type (similar to the ' σ ' bond in V.B. theory); then the two P_x atomic orbitals, as also the two p_y orbitals will overlap laterally to give M.O's of the π type.

- When electrons are successively placed in the M.O's, Aufbau principle, Hund's rule and Pauli's principle are followed, as in the case of the atomic orbitals.

Aufbau Principle : M.O's are occupied in the order of increasing energy. The following is the general arrangement of M.O's in the order of increasing energy.

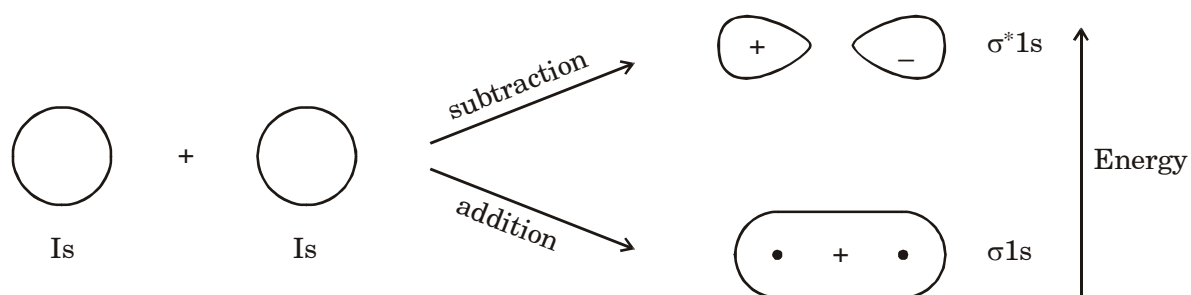
$\sigma(1s) < \sigma^*(1s) < \sigma(2s) < \sigma^*(2s) < \sigma(2p_z) < \pi(2p_x) = \pi(2p_y) < \pi^*(2p_x) = \pi^*(2p_y) < \sigma^*(2p_z)$
... etc.

The above is only a general order and slight variations often occur due to interaction between s and p orbitals. For example, sometimes, $\pi(2p_x) = \pi(2p_y) < \sigma(2p_z)$.

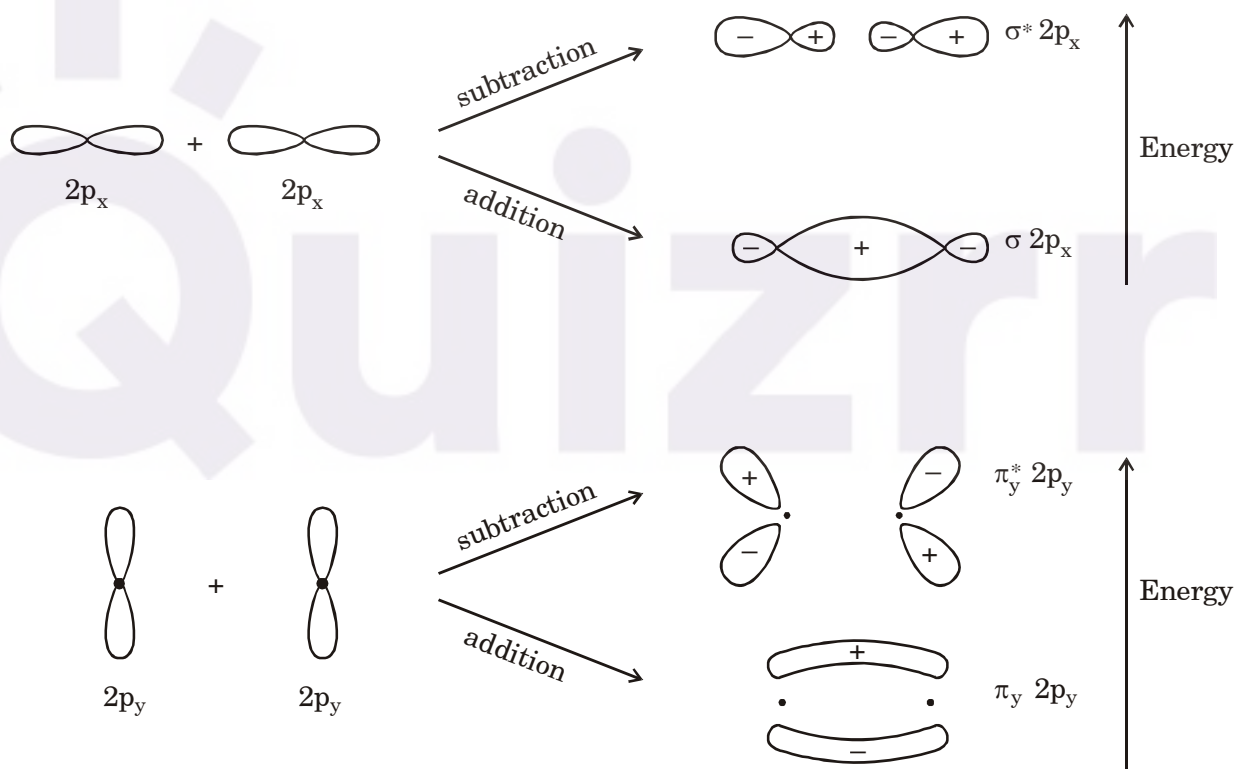
- Hund's rule of maximum multiplicity :**
The degenerate M.O's are occupied singly, before any pairing could occur. The maximum capacity for each M.O. is 2 electrons.
- Only atomic orbitals of equal or nearly equal energies combine to give the M.O's. In the case of homonuclear diatomic molecules, energies of corresponding A.O's of the two atoms are equal so the above condition of combination of A.O's assumes special significance in the case of Hetero nuclear diatomic molecules and it has to be used with caution.

Formation of molecular orbitals.

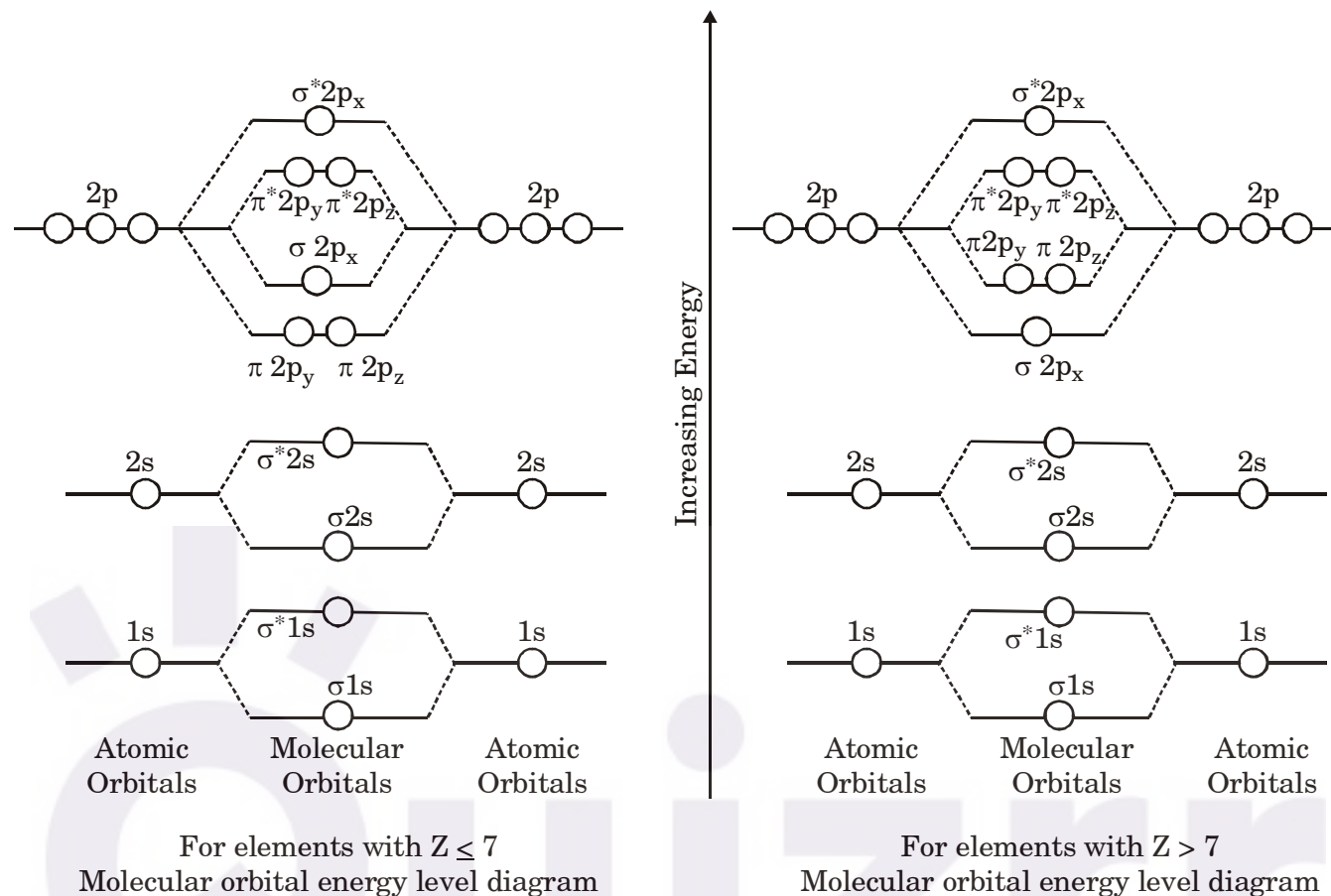
(1) From s-atomic orbitals.



(2) From p orbitals



Energy level diagram for Molecular Orbitals



BOND ORDER AND BOND STABILITY

$$\text{Bond order} = \frac{\text{No. of electrons in bonding Molecular orbitals} - \text{No. of electron in antibonding molecular orbitals}}{2}$$

- Greater the bond order, the more stable it will be. Hence,

(i) Bond energy \propto Bond order

(ii) Bond length $\propto \frac{1}{\text{Bond order}}$

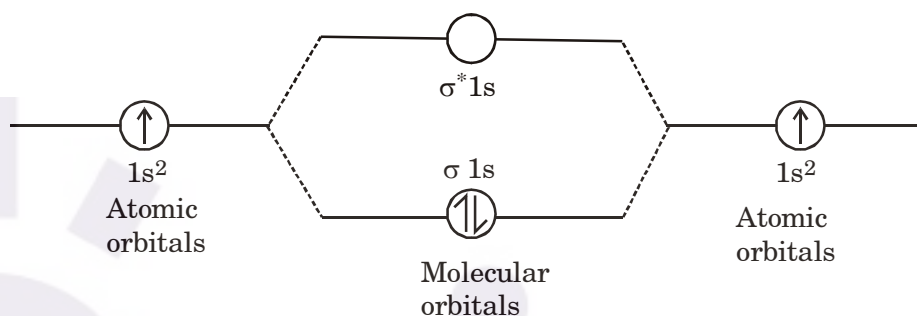
- When bond order is zero or less than zero, the species is unstable and doesnot exist.
- A bond order of +1 indicates a stable single bond.
- A bond order of +2 indicates a stable double bon.
- A bond order of +3 is a stable triple bond.

- A bond order of $+\frac{1}{2}$ shows that the species is unstable but it exists.
- If the molecule contains unpaired electrons, it will be paramagnetic and hence it is attracted in a magnetic field.
- If the molecule has all paired electrons, the molecule will be diamagnetic and hence it is repelled in the magnetic field.

Note : Fractional bond order indicates ion.

Molecular Orbital Configuration of Some homonuclear diatomic species

1. **H₂** : It is formed from 1s atomic orbitals of two atoms.

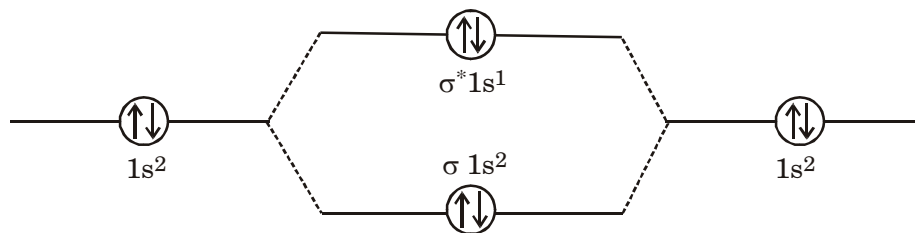


Hence, M.O. configuration of H₂ is $\sigma 1s^2$

$$\text{B.O.} = \frac{2 - 0}{2} = 1$$

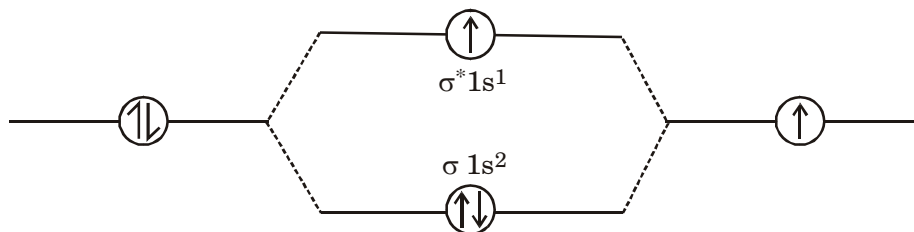
Hence it is stable and diamagnetic

2. **He₂** : Electronic configuration of He atom : $1s^2$



$$\text{B.O.} = \frac{2 - 2}{2} = 0$$

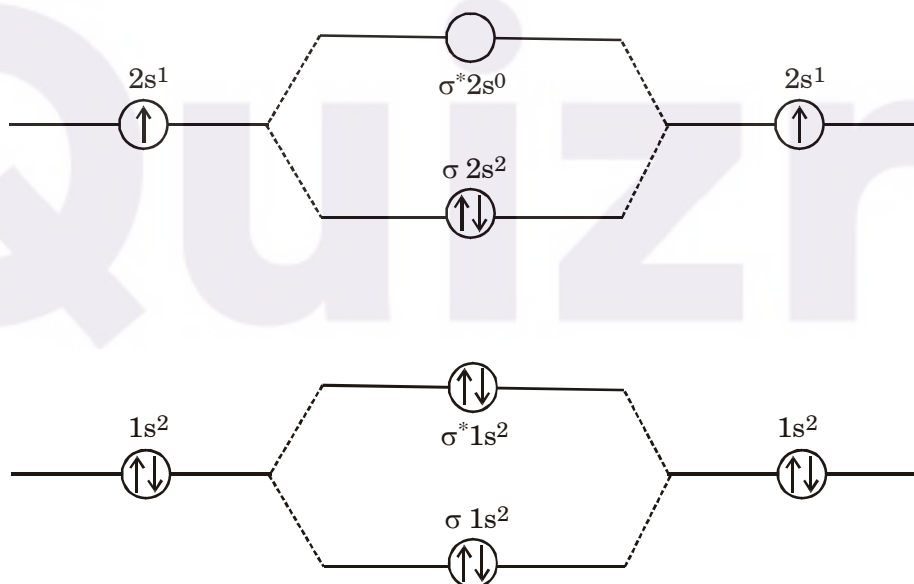
Hence He₂ is not stable.

3. He_2^+ 

the structure is $\sigma 1s^2, \sigma^* 1s^1$

$$\text{B.O.} = \frac{2 - 1}{2} = \frac{1}{2}$$

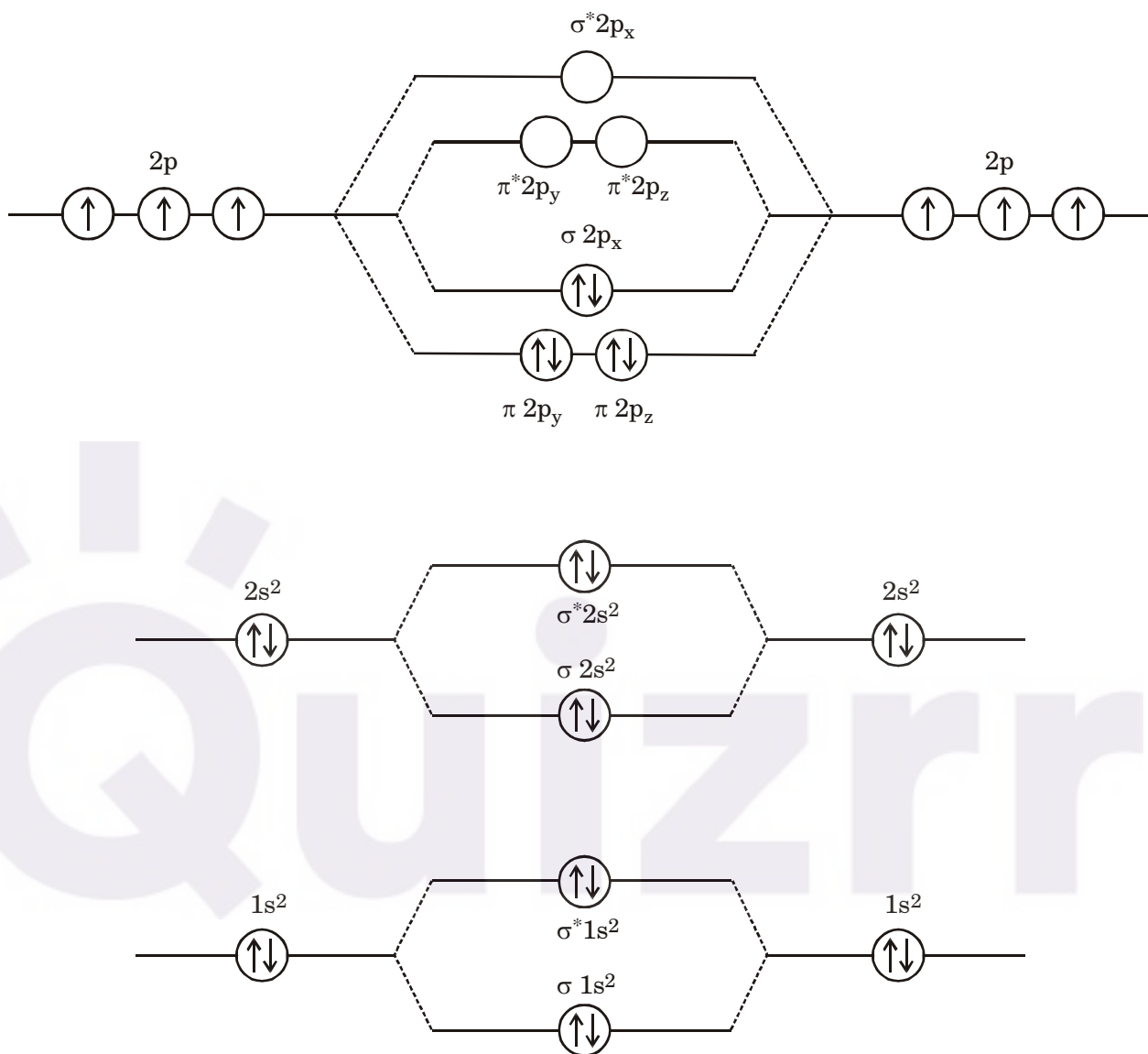
Hence, He_2^+ is stabler than He_2

4. Li_2 (Li atom : $1s^2 2s^1$)

$$\text{B.O.} = \frac{4 - 2}{2} = 1$$

hence, Li_2 is stable and is found to exist to some extent in lithium vapour.

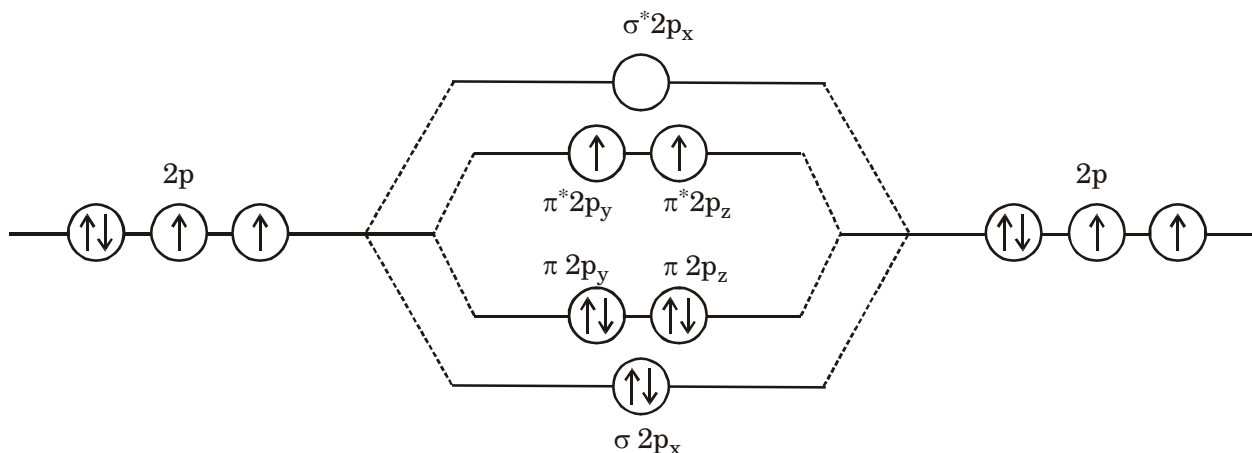
5. N_2 (N atom : $1s^2 2s^2 2p^3$)



$$\text{B.O.} = \frac{1}{2} (10 - 4) = 3$$

Thus molecule is diamagnetic and has a triple bond.

6. $O_2 : [O : 1s^2 2s^2 2p^4]$



$$\text{B.O.} = \frac{10 - 6}{2} = 2$$

Due to the presence of unpaired electrons in the two antibonding orbitals, O_2 is paramagnetic.

Let us now compare the bond strength of O_2 , O_2^+ , O_2^- , O_2^{2-} .

7. For O_2^- : one electron from the antibonding M.O. has been removed.

$$\therefore \text{B.O.} = \frac{8 - 3}{2} = 2.5$$

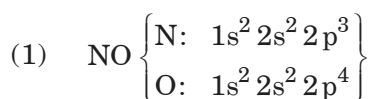
For O_2^- one electron is added to the antibonding M.O.

$$\therefore \text{B.O.} = \frac{8 - 5}{2} = 1.5$$

For O_2^{2-} $\text{B.O.} = \frac{8 - 6}{2} = 1$

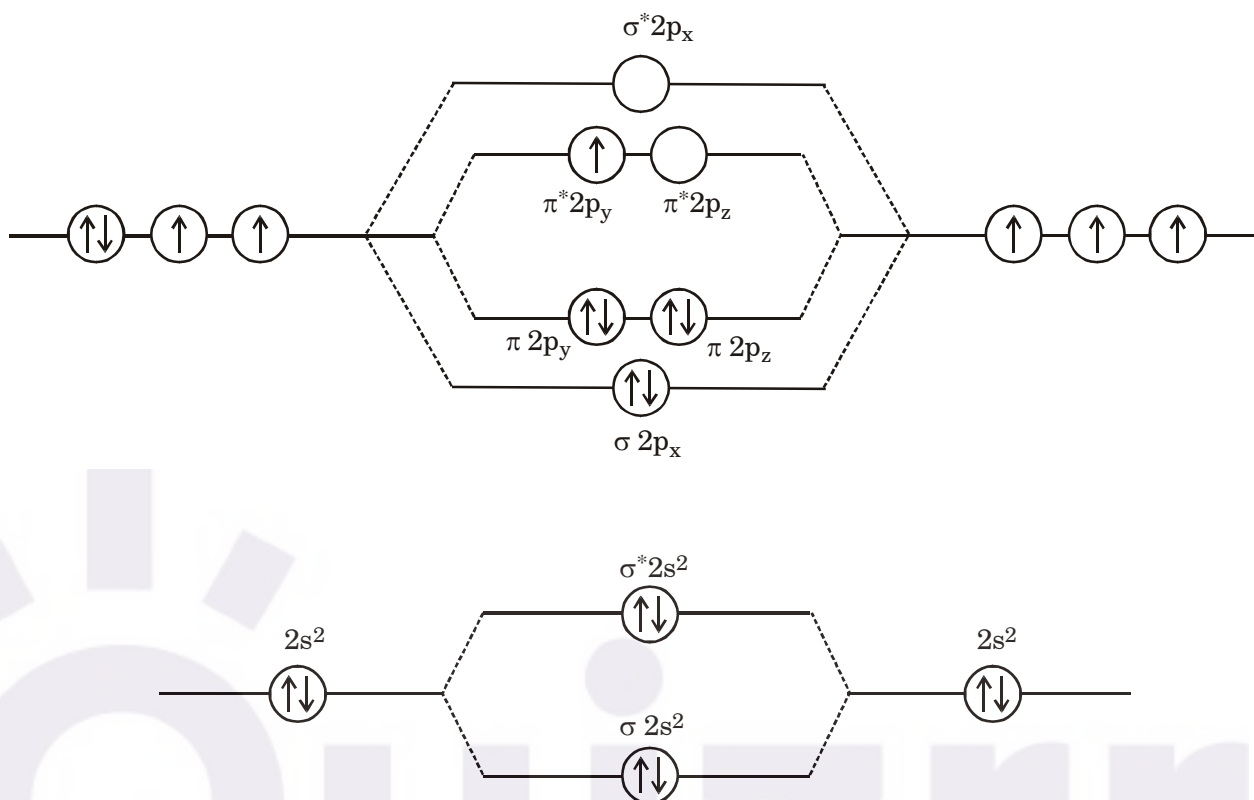
\therefore the bond is strongest in O_2^+ and the bond length the least.

HETERONUCLEAR DIATOMIC SPECIES



Total valence electrons = 5 + 6 = 11

Please note that since Oxygen is present, hence we take molecular energy diagram for $z \geq 7$
Hence,



$$\text{B.O.} = \frac{8 - 3}{2} = 2.5$$

Due to the presence of an unpaired electron in an antibonding orbital, NO is paramagnetic.

Let us compare the B.Os in NO, NO⁺, NO²⁺, NO⁻,

For NO : B.O. = 2.5

For NO⁺ : B.O. = $\frac{8 - 3}{2} = 2.5$ = (note that NO⁺ is isoelectronic with N₂)

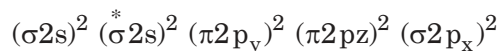
For NO²⁺ : B.O. = $\frac{7 - 2}{2} = 2.5$

[NO²⁺ is formed by removing 1e⁻ from an antibonding orbital and 1e⁻ from a bonding orbital of NO]

(2) Carbon monoxide molecule (CO)

Total valence electrons = 4 + 6 = 10

The distribution of electrons in various molecular orbitals of CO molecule is done in the following manner :



$$\text{Bond order} = \frac{1}{2} (8 - 2) = 3$$

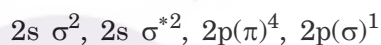
It represents one sigma bond and two π -bonds. The molecule is stable and diamagnetic in nature.

Example 11

Find the bond orders in the species, CN, CN⁻, CN⁺, F₂ and FO.

Solution :

- (a) CN. On the basis of the simple treatment of A.O overlap, the nine valence electrons (4 + 5) in CN are distributed as



$$\text{B.O.} = \frac{7 - 2}{2} = 2.5$$

- (b) CN⁻ (isoelectronic with N₂). B.O. = 3

- (c) CN⁺ (isoelectronic with C₂). B.O. = 2

- (d) F₂ : The valence (14) electrons are distributed as $2s \sigma^2, 2s \sigma^{*2}, 2s \sigma^2, 2p(\pi)^4, 2p(\pi)^{*4}$

$$\text{B. O.} = \frac{8 - 6}{2} = 1$$

- (e) FO : Number of valence electrons = 7 + 6 = 13.

The distribution may be represented as $2s \sigma^2, 2s \sigma^{*2}, 2s \sigma^2, 2p\pi^4, 2p\pi^{*3}$

$$\text{B.O.} = \frac{8 - 5}{2} = 1.5$$

Example 12

Compare the bond energies of N_2 , N_2^+ & N_2^- .

Solution :

The configuration of N_2 is

$$\sigma_{1s}^2 \sigma_{1s}^{*2} \sigma_{2s}^2 \sigma_{2s}^{*2} \left\{ \begin{array}{c} \pi_{2py} \\ \pi_{2pz} \end{array} \right\}^2 \sigma_{2px}^2 \left\{ \begin{array}{c} * \\ \pi_{2py} \\ \pi_{2pz} \end{array} \right\}$$

Now N_2^+ means removal of an electron from a bonding M.O. This will decrease the B.O.

$$\therefore \text{B.O. of } N_2^+ = \frac{1}{2}(5 - 0) = 2.5$$

Now again for N_2^- bond order is $\frac{1}{2}(6 - 1) = 2.5$

So from the bond order it may seem that both N_2^+ & N_2^- may have the same bond energy. But removal of an electron from a diatomic species tend to decrease the inter electronic repulsion and thereby shortens the bond lengths. So the bond energy becomes more than compared to N_2^- .

$$\therefore N_2 > N_2^+ > N_2^-$$

Example 13

Compare the bond length of O-O in following molecules :

KO_2 , O_2 , $O_2[AsF_6]$

Solution :

KO_2 has O_2^-

$O_2[AsF_6]$ has O_2^+ Bond order = 2.5

O_2 : Bond order = 2

Bond length in increasing order.

$$O_2^+ < O_2 < O_2^-$$

Example 14

Which diatomic molecule of second period besides O_2 should be paramagnetic?

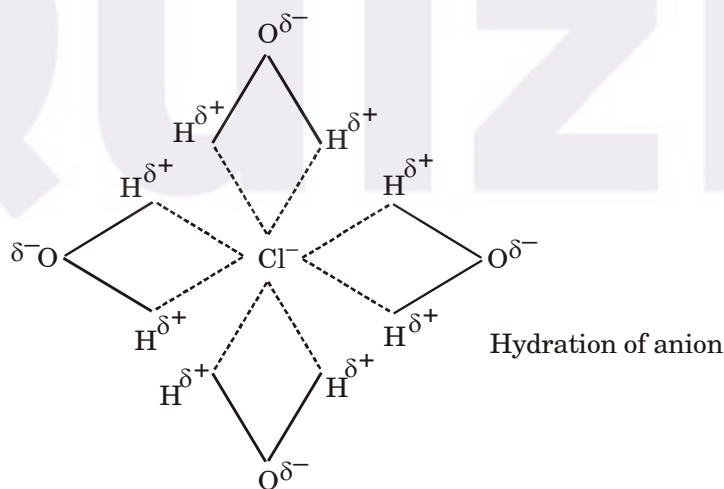
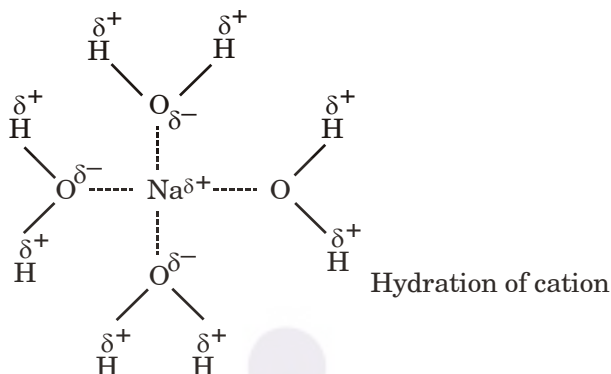
Solution :

$$B_2 - (\sigma_{1s})^2 (\sigma_{1s}^*)^2 (\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\sigma_{2p_x})^2 (\pi_{2p_y})^2 = (\pi_{2p_z})^2 (\pi_{2p_z}^*)^1 = (\pi_{2p_y}^*)^1 (\sigma_{2p_x})^0$$

As, paramagnetism arises due to unpaired electron. Therefore B_2 is paramagnetic molecule.

Consider a sample of Cl_2 . The electron cloud around chlorine atoms is not stationary. It vibrates so, sometimes, one chlorine atom may attract it more than the other, leading to sudden appearance of partial positive and negative charges. Now, one molecule is surrounded by millions of other molecules. Whenever the instantaneous dipoles are suitably oriented (positive pole of one close to negative pole of other), it leads to weak force of interaction which are called induced dipole-induced dipole interaction.

- (4) **Ion-dipole interaction :** This type of interaction can be suitably explained using the dissolution of NaCl in H_2O . The +vely charged Na^+ ions are attracted by the oxygen atoms and Cl^- by the hydrogen atom of H_2O . It is called hydration.



In hydration, energy is liberated due to attraction among oppositely charged ions and energy of the system is lowered. This energy is called **heat of hydration** or **hydration energy**.

Cation having smaller size will have higher hydration energy because charge density will be higher. Relative magnitude of the above forces.

Induced dipole-induced dipole < Dipole-induced dipole < Dipole – dipole < Ion – dipole

13. HYDROGEN BONDING

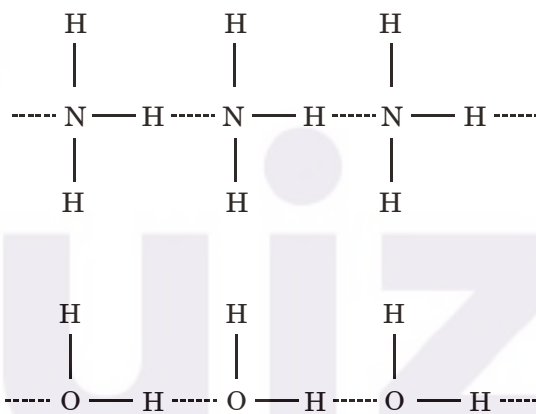
It is an electrostatic attractive force between covalently bonded hydrogen atom of one molecule or a part of a molecule and an electro negative atom (such as F, O, N) of another molecule or another part of the same molecule. It is very weak (strength about 2-10 kcal mol⁻¹ or 8.4 – 42 kJ mol⁻¹) as compared to a covalent bond (strength 50–100 kcal mol⁻¹ or 209–418.4 kJ mol⁻¹).

Conditions for Hydrogen Bonding

1. The molecule must possess a highly electronegative atom linked to hydrogen atom.
2. The size of the electronegative atom should be small.

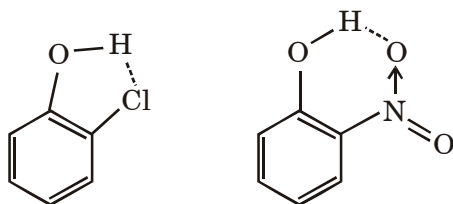
Types of Hydrogen Bonding

1. **Inter-Molecular Hydrogen Bonding :** In this, two molecules of the same compound join to form aggregates. For example,



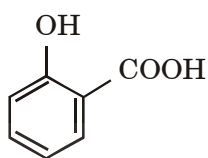
Intermolecular hydrogen bonding increases the boiling point of the compound and also its solubility in water.

2. **Intramolecular Hydrogen Bonding :** In this hydrogen occurs between atoms of the same molecules present on different sites. This leads to intramolecular ring formation and this phenomenon is called **chelation**. Some examples are :

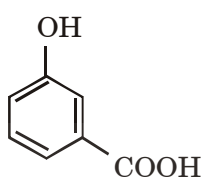


9.3 Consequences of hydrogen bonding

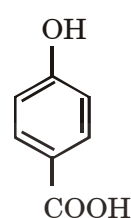
- High boiling and melting points of NH_3 , H_2O and HI in comparison to hydrides of other elements of V, VI and VII groups to which N, O and F belong respectively are due to hydrogen bonding.
- Unique properties of water and ice are due to hydrogen bonding. Density of ice is less than water and water contracts when heated between 0 C to 4 C. These two unique properties are explained on account of open cage structure of ice due to hydrogen bonding.
- Strength of certain acids and bases can be explained on the basis of hydrogen bonding eg. when we compare the acidic strength of o - m - and p - hydroxy benzoic acid.



$$K_a = 10.5 \times 10^{-5}$$



$$K_a = 8.3 \times 10^{-5}$$



$$K_a = 2.9 \times 10^{-5}$$

The abnormally high dissociation constant of o - hydroxybenzoic acid is due to the fact that the conjugate base is stabilised by hydrogen bonding.

- Solubility :** The organic compounds like alkane, alkenes, alkynes are insoluble in water due to absence of H-bonding whereas alcohols, organic acids, amines are soluble in water due to H-bonding.
- State of matter :** H_2O exists in liquid state whereas H_2S in gaseous state because hydrogen bonding exist in water and no H-bonding exists in H_2S .

INERT PAIR EFFECT

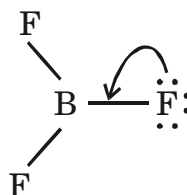
Heavier p-block and d-block elements show two oxidation states. One is equal to group number and second is group number minus two. Fore example.

Pb ($5s^2$, $5p^2$) shows two oxidation states, + II and + IV. Here + II is more stable than +IV. Here +II is more stable than +IV which arises after loss of all four valence electrons. Reason for more stability of +II O.S. is that $5s^2$ electrons are reluctant to participate in bonding because bond energy released after bond formation is less than that required to unpair these electrons.

BACK BONDING

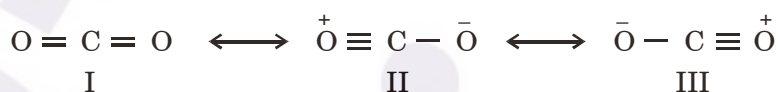
Sometimes, in order to make up electron deficiency in the central atom, the surrounding atom forms a π -bond which is one side, i.e. shared electrons are contributed by surrounding atom only

which is having lone pair of electrons. Overlap involves vacant orbital on the central atom and filled orbital on surrounding atom.



RESONANCE

It is generally observed that a single valence bond structure of a molecule cannot correctly account for the properties of the molecule. In such cases, the concept of resonance is introduced. According to this concept if two or more alternate valence bond structures can be written for a molecule, the actual structure is said to be a resonance or mesomeric hybrid of all these alternate structures. For example, carbon dioxide molecule can be represented by the following three structures :



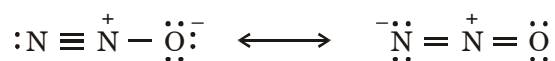
The calculated values of bond distances between carbon and oxygen in $\text{C} = \text{O}$ and $\text{C} \equiv \text{O}$ are 1.22 Å and 1.10 Å, respectively but the observed bond distance between carbon and oxygen in carbon dioxide is 1.15 Å. Thus, none of the above structures correctly explains the observed bond length. It is, thus, said that a hybrid form of these structures can provide the exact explanation. The various structures of which the molecule is a resonance hybrid are known as canonical forms or mesomeric forms. Actually resonance hybrid does not oscillate between the canonical forms of a mixture of these forms but it is a definite form and has a definite structure which cannot be written on paper.

Rules for Selecting Canonical Forms or Mesomeric Forms :

- The relative position of all the atoms in each of the canonical forms must be the same. They should differ only in the position of electrons.
- The number of unpaired and paired electrons in each of the canonical forms must be same.
- The contributing structures should not differ much in energy.
- The contributing structures should be such that negative charge resides on more electronegative and positive charge on the electropositive. Like charges should not reside on atoms close together in the canonical forms.

Formal charges on the atoms in the molecule help us in choosing the most appropriate resonance structure. For example, nitrous oxide molecule is represented by two resonance

electron dot structures, one of which has a negative formal charge on the oxygen atom and the other of which has a negative charge on the terminal nitrogen atom.

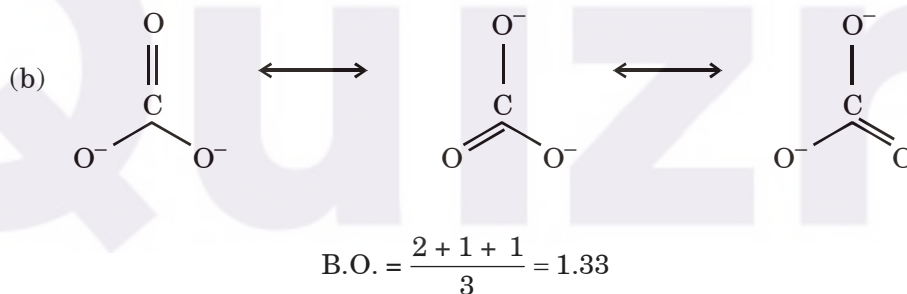
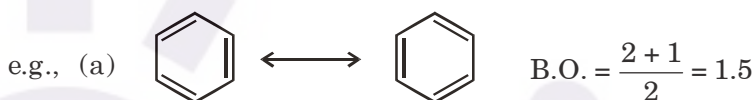


Since oxygen is a more electronegative element than nitrogen, the structure that places a negative formal charge on oxygen is probably lower in energy than the structure that has a negative formal charge on nitrogen.

Thus, the actual structure of N_2O is $:\text{N} \equiv \overset{+}{\text{N}} - \ddot{\underset{-}{\text{O}}}$

- (v) As a result of resonance, the bond order changes in many molecules or ions.

$$\text{Bond order} = \frac{\text{Total number of bonds between two atoms in all the structures}}{\text{Total number of resonating structures}}$$



Resonance Energy

It has been observed that the molecule which shows resonance has greater heat of formation than the calculated heat of formation of any one of canonical forms. The difference is represented by ΔE and its called resonance energy.

$$\Delta E = \left(\text{Experimental value of heat of formation} \right) - \left(\text{Calculated value of heat of formation of most stable canonical form} \right)$$

On account of ΔE , the hybrid form is more stable than any of the canonical forms.

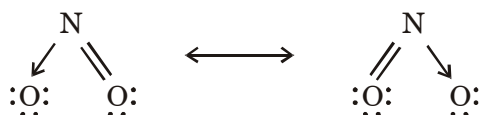
Energy difference between most stable resonating structure and resonance hybrid structure is called resonance energy.

Some Examples showing Resonance

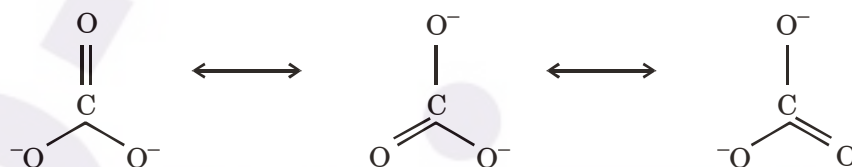
(i) **Nitric oxide molecule** : It is a resonance hybrid of following two structures :



(ii) **Nitrogen dioxide molecule** : It is a resonance hybrid of the following structures :



(iii) **Carbonate ion** : it is the resonance hybrid of the following forms :



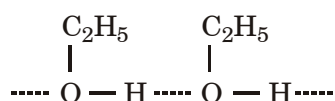
MISCELLANEOUS EXAMPLES

Example 1

Ethyl alcohol ($\text{C}_2\text{H}_5\text{OH}$) has higher boiling point than dimethyl ether ($\text{CH}_3\text{-O-CH}_3$) although the molecular weight of both are same.

Solution :

Though ethyl alcohol and dimethyl ether have the same molecular weight but in ethyl alcohol the hydrogen of the O-H groups forms intermolecular hydrogen bonding with the OH group in another molecule. But in case of ether the hydrogen is linked to C is not so electronegative to encourage the hydrogen to form hydrogen bonding.



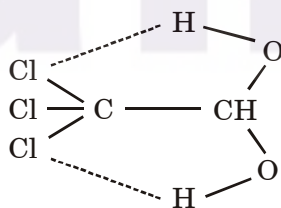
Due to intermolecular H-bonding, ethyl alcohol remains in the associated form and therefore boils at a higher temperature compared to dimethyl ether.

Example 2

Explain unusual stability of chlorohydrate through a compound with two or more-OH groups present on one carbon atom is usually unstable.

Solution :

The unusual stability of chloral hydrate has been attributed to $-\text{I}$ effect of chlorine and to the formation of interamolecular hydrogen bonds.



Example 3

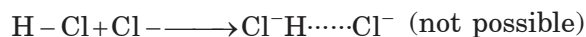
The salt KHF_2 is known but KClF_2 is not known. Explain.

Solution :

The formation of KHF_2 involves reaction of HF_2^- with KOH . Similar is the case with KClF_2 .

So the main factor is the formation of HF_2^- or HClF_2^- ion.





Due to higher electronegativity and small size of fluorine, it is capable of forming H-bond resulting in the formation of HF_2^- and thereby KHF_2 exists. But with chlorine, there is no possibility of H-bonding, so there is no possibility of existence of KHC l_2 .

Example 4

o-hydroxy benzaldehyde is more volatile than p-hydroxy benzaldehyde.

Solution :

More volatility means compound has lower boiling point. p-hydroxy benzaldehyde remains associated through intermolecular hydrogen bonding. But in o-hydroxy benzaldehyde, intramolecular H-bonding takes places, as a result of which there is no association. So p-hydroxy benzaldehyde, which remains as an associated species has got higher boiling and so less volatile while o-hydroxy benzaldehyde is highly volatile.

Example 5

Though the electronegativities of nitrogen and chlorine are same, NH_3 exists as liquid whereas HCl as gas. Why ?

Solution :

The size of nitrogen is less than the size of chlorine. Therefore, electron density in nitrogen is more than that of chlorine. So, nitrogen forms hydrogen bonding leading to association of molecules. Hence, NH_3 is liquid. Hydrogen bonding is not possible with chlorine.

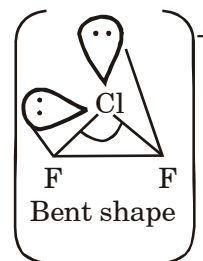
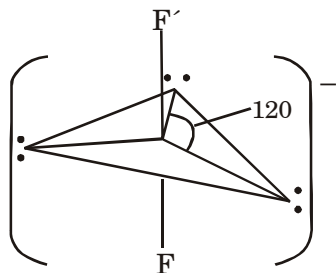
Example 6

Explain giving reason :

ClF_2^- linear, but the ion ClF_2^+ is bent.

Solution :

In ClF_2^- central chlorine atom involves sp^3d hybridization, to have minimum electronic repulsion three lone pairs should be in equatorial position as follows; giving linear shape to the ion. Whereas, in case of ClF_2^+ ion central atom Cl involves sp^3 hybridization having two lone pairs, resulting in bent shape for the ion, (bond angle less than $109^\circ 28'$ due to repulsion of bond pair by lone pair).



Example 7

Arrange in order of increasing dipole moment BF_3 , H_2S , H_2O

Solution :

BF_3 has zero dipole moment because of symmetry, H_2S has a lower dipole moment than H_2O because of much lower bond polarity of H-S bond compared to H-O bond. Hence the order is $\text{BF}_3 < \text{H}_2\text{S} < \text{H}_2\text{O}$.

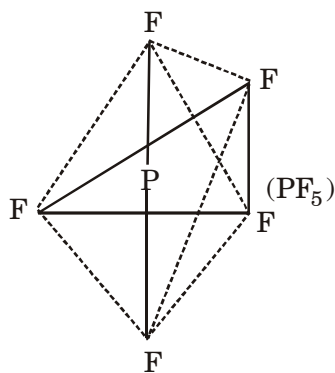
Example 8

Explain with reason :

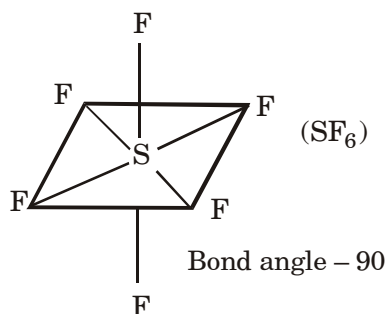
- (i) Two different bond lengths are observed in PF_5 but only one bond length observed in SF_6 .
- (ii) O-hydroxy benzaldehyde is liquid at room temperature while p-hydroxy benzaldehyde is high melting solid.

Solution :

- (i) PF_5 has trigonal bipyramidal structures (sp^3d hybridization of central atom) in which bond angles are 90° and 120° respectively and there are two types of bond-axial and equatorial (axial being longer than equatorial). In case of SF_6 the structure is octahedral (sp^3d^2 hybridization of the central atom-S) resulting only one type of bond, bond angle (90°) and one type of bond length.

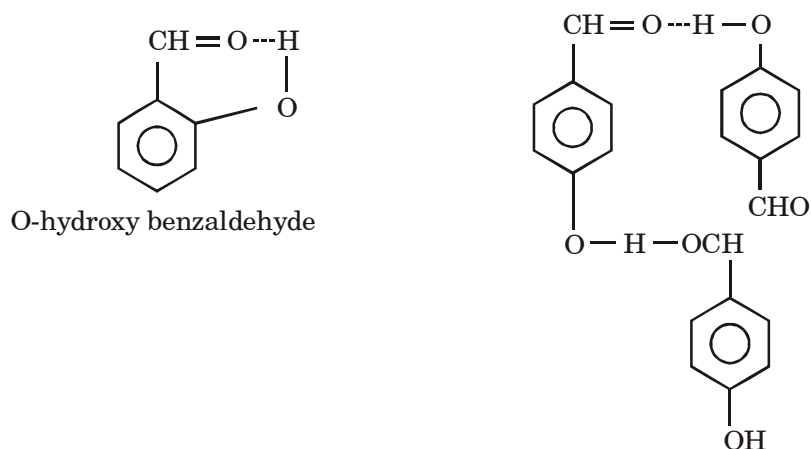


(Bond angle 90° & 120°)



Bond angle – 90°

- (ii) There is intramolecular H bonding in o-hydroxy benzaldehyde while intermolecular hydrogen bonding in p-hydroxy benzaldehyde.



Example 9

CO₂ is a gas whereas SiO₂ is solid at room temperature. Explain.

Solution :



In CO₂, pπ-pπ overlap is possible due to shorter C – O bond length and similarity in energy between the orbitals of carbon and oxygen. But in SiO₂ π-overlap is not possible and thereby to complete the octet Si has to go for intermolecular multiplicity, i.e. to form 4-sigma bonds with oxygen, hence it has high melting point.

Example 10

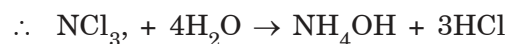
Explain the following :

- NF₃ is inert towards hydrolysis, but NC₃ undergoes hydrolysis rapidly, why ?**
- Syn-form of pyridine-2-carboxaldoxime is less stable than that of the anti-form. Why?**

Solution :

- For hydrolysis, either the central atom, or the atom around the central must contain vacant d-orbitals.

In NF₃, neither N nor F contains vacant d-orbitals, therefore it will not undergo hydrolysis. But in NCl₃, Cl atom contains vacant d-orbital. Therefore, it will undergo hydrolysis.

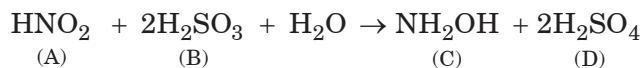


- Anti-form of pyridine-2-carboxaldoxime, has intramolecular H-bond, but the syn-form of pyridine-2-carboxaldoxime does not have intramolecular H-bond. Hence, syn form is more stable.

Example 11

In the equation, $A + 2B + H_2O \longrightarrow C + 2D$ ($A = HNO_2$, $B = H_2SO_3$, $C = NH_2OH$), identify D. Draw the structures of A, B, and D.

Solution :



Structures— (A) HNO_2 ; $HO - N = O$,

(B) H_2SO_3 ; $HO - \underset{\substack{| \\ OH}}{S} \rightarrow O$,

(C) NH_2OH ; $H - \underset{\substack{| \\ H}}{N} - OH$

(D) H_2SO_4 ; $HO - \underset{\substack{| \\ OH}}{S} \begin{matrix} \nearrow O \\ \searrow O \end{matrix}$

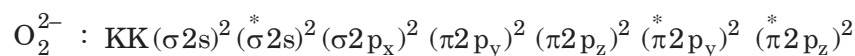
Example 12

Which of the two peroxide ion or superoxide ion has larger bond length ?

Solution :

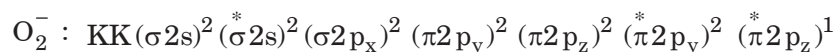
The bond length in a molecule is dependent on bond order. The higher is the bond order, smaller will be the bond length.

Peroxide ion, O_2^{2-}



$$\text{Bond order} = \frac{8 - 6}{2} = 1$$

Superoxide ion, O_2^-



$$\text{Bond order} = \frac{8 - 5}{2} = 1.5$$

Bond order of superoxide ion is higher than peroxide ion, hence bond length of peroxide ion is larger.

Example 13

Which d-orbital is involved in dsp^2 – hybridization?

Solution :

$d_{x^2-y^2}$. This is because its four lobes lie along the x-axis and y-axis. The two p-orbitals can combine along these axes.

Example 14

(i) **Arrange the following as indicated:**

- (a) NH_3 , PH_3 , AsH_3 , SbH_3 (increasing bond angle)
 (b) MgCO_3 , BaCO_3 , CaCO_3 , BeCO_3 (increasing stability)

Solution :

- (i) (a) $\text{NH}_3 < \text{PH}_3 < \text{AsH}_3 < \text{SbH}_3$
 (b) $\text{BeCO}_3 < \text{MgCO}_3 < \text{CaCO}_3 < \text{BaCO}_3$

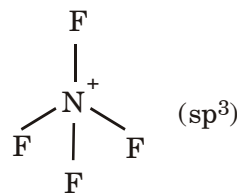
Example 15

Give the structures of compounds and hybridization of central atom in each of the following species.

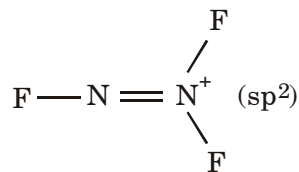
- (a) NF_4^+ (b) N_2F_3^+ (c) NH_2OH (d) SPCl_3 (e) PF_3Cl_2

Solution :

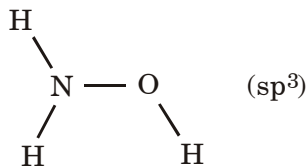
- (a) Tetrahedral



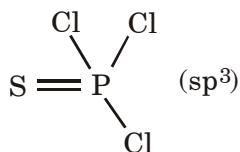
- (b) Planar at each nitrogen atom



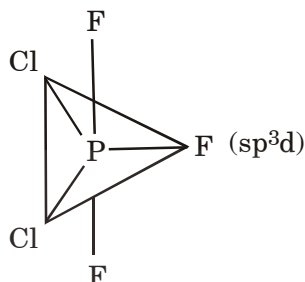
- (c) Pyramidal at N and bent at O



- (d) Tetrahedral



- (e) Trigonal bipyramidal

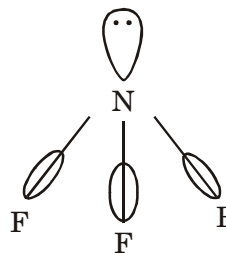
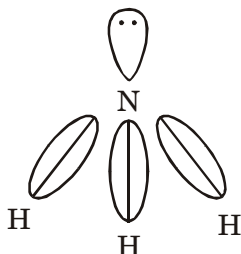


Example 16

- (a) Why is the bond energy of P-Cl bond different in PCl_3 and PCl_5 ?
 (b) Out of CH_3Cl and $CHCl_3$, which one will have higher dipole moment and why ?
 (c) Bond angle in NH_3 is greater than NF_3 whereas the bond angle in PH_3 is lesser than PF_3 . Why ?

Solution :

- (a) In PCl_3 , P exhibits sp^3 hybridization and molecule is triangular pyramidal. But in PCl_5 , P exhibits sp^3d hybridization. Therefore, it is trigonal bipyramidal. Three P-Cl bonds are on the plane while two P-Cl bonds are above and below the plane which are different from remaining three P-Cl bonds.
- (b) CH_3Cl is having higher dipole moment in comparison to $CHCl_3$. Because in $CHCl_3$, each C-Cl bond dipole induces an opposite dipole on the other two C-Cl bonds. Each C-Cl moment is thereby reduced, ultimately lowering the overall dipole moment of the molecule.
- (c) In case of NF_3 , F atoms are highly electronegative because of which the charge cloud is displaced further away from the central atom and repulsion decreases, thereby reducing the bond angle.



In case of PF_3 , the valence shell of phosphorus atom is incompletely filled. The high charge density of electron on the F atom causes a partial-shift of its lone pairs to the phosphorus atom via pi-bond formation. The P-F bonds attain some double bond character resulting in increased bp-bp repulsion thereby increasing F-P-F bond angle. This is not possible in case of NF_3 because of non-availability of vacant d-orbitals on nitrogen.

Example 17

Why H_2O is liquid while H_2S is a gas at ordinary temperature ?

Solution :

Oxygen has high electronegativity than sulphur. As a result, H_2O forms hydrogen bonding. Consequently, molecules of water come nearer to each other through hydrogen bonding. This results in higher boiling point of water and hence it is a liquid.

Example 18

The density of ice is less than that of water or ice floats over water. Explain.

Solution :

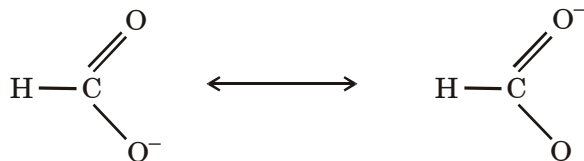
In ice, water molecule is associated with four other molecules through hydrogen bonding in a tetrahedral manner, i.e., it has open-cage like structure in which lesser molecules are packed per mL. When ice melts, the molecules come closer to one another. Consequently the density of water in liquid state is more than in solid state. Thus, ice floats over water.

Example 19

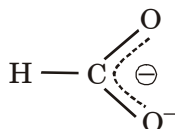
Both carbon-oxygen bonds in the methanoate ion, HCOO^- , have the same length (127 pm). What does this tell about bonding ?

Solution :

This is due to the presence of resonance in the molecule.



Each bond has part of the character of single bond and part of character of a double bond. The electrons are delocalised over the three atoms.



Example 20

The dipole moment of LiH is 1.964×10^{-29} cm and the interatomic distance between Li and H in this molecule is 596 Å. What is the per cent ionic character in LiH ?

Solution :

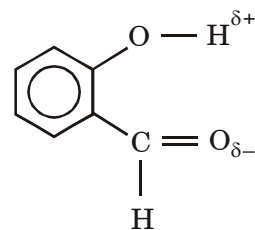
$$\begin{aligned} \text{The dipole moment of 100\% ionic molecule (Li}^+\text{H}^-) &= (1 \text{ electronic charge}) (\text{interatomic distance}) \\ &= (1.602 \times 10^{-19} \text{ C}) (5.96 \times 10^{-10} \text{ m}) \\ &= 2.557 \times 10^{-29} \text{ Cm} \end{aligned}$$

Fractional ionic character

$$= \frac{\text{Exp. value of dipole moment}}{\text{Theoretical value of dipole moment}}$$

$$= \frac{1.964 \times 10^{-29}}{2.557 \times 10^{-29}} = 0.768$$

The bond in LiH is 76.8% ionic.



(o-hydroxybenzaldehyde)
Intrahydrogen bonding

Example 21

Discuss the hybridization of carbon atoms in allene (C_3H_4) and show the p-orbital overlaps.

[I.I.T. 1999]

Solution :

Allene is $\text{CH}_2 = \text{C} = \text{CH}_2$ carbon atoms I and III are in sp^2 hybridized state while carbon II is in sp hybridized state. Two unhybridized orbitals of carbon II overlap sidewise with unhybridized orbital of each of carbon I and carbon III to form π -bonds besides it also forms a sigma bond with each of the carbon atoms using hybridized orbitals. Two hybridized orbitals of each of carbon I and III form sigma bonds with hydrogen atoms.

