CHAPTER – 4

CHEMICAL BONDING

4.1 ENERGETICS OF BOND FORMATION

A molecule as compared to the atoms from which it is formed is more stable because it possesses energy lower than the energy of the uncombined atoms. This difference in energy is due to the fact that when atoms combine to form molecule, the attractive forces are created which result in the release of energy. *The attractive force that holds atoms together in a compound is known as the chemical bond.*

The force of attraction or chemical bond between two atoms is formed due to the interaction of valence electrons of combining atoms.

In 1916 two kinds of chemical bonds were described: *The ionic bond by* W. Kossel (Germany) and *Covalent* bond by G. N. Lewis (U.S.A.). Both these chemists based their ideas on the fact that atoms attain greatest stability when they acquire an inert gas electronic configuration (Octet Rule). As a matter of fact atoms of the inert gases have eight electrons in their outermost orbit, excepting helium which has only two electrons. These gases are very stable and do not enter into chemical combination under ordinary conditions and therefore they are assumed to have stable orbits. Atoms of all the other elements have incomplete outermost orbits and tend to complete them by chemical combination with the other atoms. This inert gas configuration can be achieved either by the transference or sharing of electrons among themselves. It is the tendency of atoms to acquire inert gas configuration which causes the atoms to form chemical bonds.

4.2 ELECTROVALENT OR IONIC BOND

This type of chemical bond proposed by Kossel is formed as a result of complete transference of one or more electrons from one atom to the other so that both the atoms acquire inert gas configuration (the octet rule). The atom that loses electrons becomes positively charged and the atom that gains electrons becomes negatively charged. The charged atoms (called ions) so produced are held together by electrostatic force of attraction. The ionic bond is, therefore, defined as *the electrostatic attraction between positive and negative ions.*

Ionic compounds such as NaCl and MgO are formed by the elements of low electronegativity (metals) and the elements of high electronegativity (non-metals). If difference in electronegativity, ΔE.N, is greater than 1.7 between two elements usually leads to an ionic bond.

The metal of groups IA, IIA and Aluminium in IIIA due to their low ionization potential and low electronegativity, lose one, two or three electrons to form M^{+}, M^{2+} and M^{3+} ions respectively. The non-metals of groups VIA and VIIA due to their high electron affinity and high electronegativity tend to gain two electrons and one electron to form A^{2-} and A^{1-} ions respectively. Nitrogen and phosphorus in VA group will under some circumstances gain three electrons to form N^{3-} (Nitride) and P^{-3} (Phosphides) ions

In order to understand why ionic bonds are formed readily between the metals and non-metals of the above mentioned groups, let us consider the energy changes involved in the formation of say, sodium chloride from sodium and chlorine atoms.

(i) Sodium in the ground state has the electronic configuration of $1s^2, 2s^2, 2p^6$ $3s^1$, i.e. it has one valence electron. The loss of the valence electron requires 495 KJ mole^{-1}, the resulting Na^{+} has complete octet.

$$\underset{\substack{1s^2,\,2s^2,\,2p^6,\,3s^1\\(11\bar{e})}}{Na_{(\omega)}} \xrightarrow{\qquad\qquad} \underset{\substack{1s^2,\,2s^2,\,2p^6\\(10\bar{e})}}{Na^{+}_{(\omega)} + e^{-}} \qquad \Delta H = +495 \text{ KJ/mole}$$

(ii) Chlorine atom in its ground state has the electronic configuration of $Is^2, 2s^2, 2p^6, 3s^2, 3p^5$, that is, it needs one more electron to complete its octet. The gain of one electron by chlorine releases energy which is equal to 348 KJ mole^{-1}.

$$Cl_{(g)} + e^- \longrightarrow Cl^-_{(g)} \qquad \Delta H = -348 \text{ KJ/mole}$$

$$\underset{(17\ e^-)}{1s^2, 2s^2, 2p^6, 3s^2, 3p^5} \qquad \underset{(18\ e^-)}{1s^2, 2s^2, 2p^6, 3s^2, 3p^6}$$

The energy difference (495-348=147KJ/mole) is more than compensated when the oppositely charged ions form a crystal lattice consisting of a closely packed array, in which each ion is surrounded by six opposite ions (Fig. 4.1) The great attractive forces in the crystal lattice greatly reduce the energy of the system there by making it stable. Thus the more important step is the third step which involves the formation of crystal lattice.

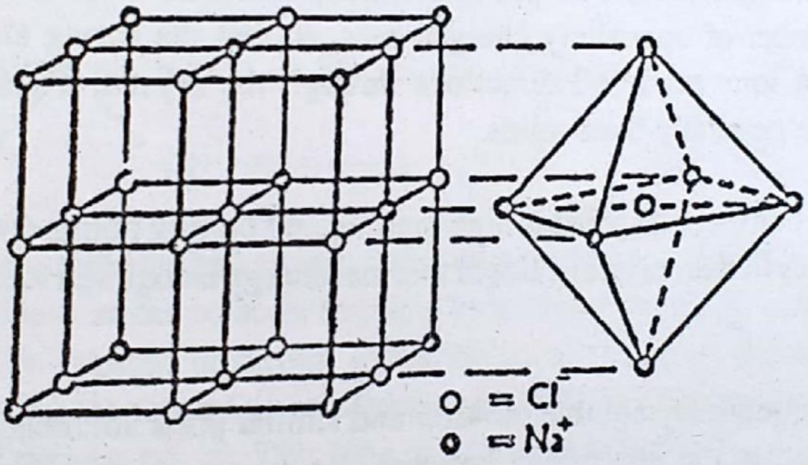


FIGURE 4.1
Crystal structure of sodium chloride, showing (right) the octahedral arrangement of six sodium ions around one chloride ion.

(iii) $Na^+_{(g)} + Cl^-_{(g)} \rightarrow Na^+Cl^-_{(s)}$ $\qquad \Delta H = -788.0$ KJ/mol

The energy released when one mole of gaseous ions arrange themselves in definite pattern to form crystal lattice is referred to as the lattice energy. It is this energy which over comes the loss of energy encountered in the formation of the ions.

From the above discussion, we conclude that it is essential for the formation of ions and the ionic bond that the sum of the energies released in the second and third steps must be larger than what is required in the first step.

Characteristics of Ionic Compounds

(i) A single ion of a metal is never associated with a single ion of non-metal i.e. separate units of ionic compounds do not exist and therefore it is wrong to talk about a molecule of an ionic compound. The formula only indicates the relative number of atoms of each element. The solid crystal is made up of large number of oppositely charged ions, arranged in definite pattern. Each ion is surrounded by a fixed number of oppositely charged ions, so that the strong electrostatic forces between ions act in all directions through the crystal. Thus the ionic compounds are generally hard solids.

(ii) The ionic compounds possess high melting and boiling points due to strong inter ionic forces in their crystals. Lot of thermal energy is required to break those forces.

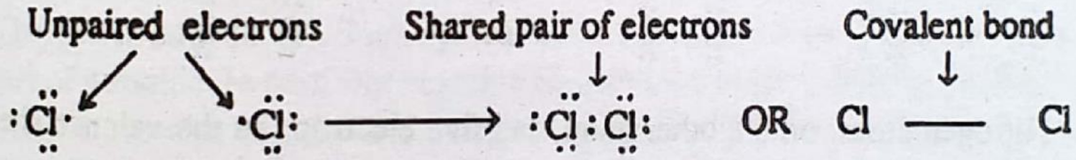
(iii) Ionic compounds are soluble in water and similar polar solvents because of the strong electrostatic attractions between the ions and polar molecules of solvent. The surrounding of the ions by the solvent molecules solvation releases the energy which is known as the energy of solvation. This energy usually overcomes the high lattice energy of the ionic compound.

Insoluble ionic compounds (e.g. the sulphates, phosphates and fluorides of Ca, Sr and Ba) have very high lattice energies and insufficient solvation energy is available from the ions to overcome the high lattice energies for these compounds to be soluble. The ionic compounds are insoluble in the organic solvents like Benzene, carbon tetrachloride etc. because there is no attraction between the ions of ionic compounds and the molecules of non polar solvents.

(iv) Ionic componds are invariably electrolytes, because in the presence of a polar solvent such as water, the interionic forces are so weakened that the ions are separated and the free ions are able to move under the influence of electric current. In fact the ionic compounds conduct electricity even in the fused or melted state.

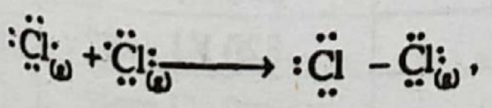
4.3 COVALENT BOND

The atoms in an ionic compound are held together by the transfer of valence electron or electrons from one atom to the other atom. In covalent bonding, no such transfer is involved, instead two atoms both of which tend to gain electrons may combine with each other by sharing one or more pairs of electrons. This concept of electron pair bond was proposed by G.N. Lewis in 1916. Two atoms of chlorine for instance, each having seven electrons in its valence shell unite by sharing two of these fourteen electrons between them. This is shown diagramatically as follows, using dots to indicate only the valence electrons:



Electrons that are shared between two atoms are the bonding electrons and are to be counted toward the octet (or duplet in case of hydrogen) of each of the bonding atom. As the shared electrons spend much of the time between the nuclei, resulting in the attractive forces between negative charge of electrons and positive charges of the two nuclei. This type of chemical bonding is known as covalent bond.

In chlorine molecule, for instance, the one shared pair of electrons forms a single covalent bond between two chlorine atoms (Cl — Cl). The sharing of electrons in a covalent bond brings the bonded atoms closer together which is reflected from the bond energy data of the bonds. For example, when two chlorine atoms form a single covalent bond, 242 KJ/mole of energy are released.



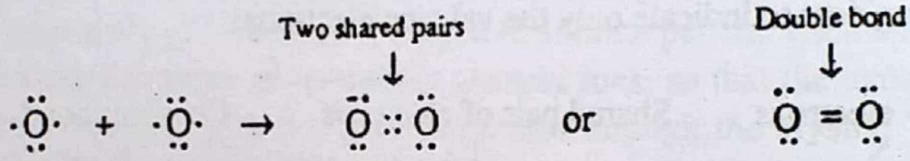
$\Delta H = -242 \text{ KJ mol}^{-1}$

The release of energy lowers the energy of the molecule and thus makes it more stable.

Another normal feature of a single covalent bond is that the spins of the bond forming electrons, unpaired with separate atoms, becomes paired in the bond formation.

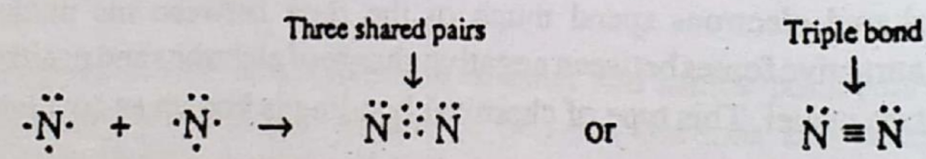
In addition to single covalent bond as mentioned in Cl_2 molecule, atoms also form multiple bonds, that is, double and triple bonds as in case of Oxygen and Nitrogen molecules.

An oxygen atom has six valence electrons, therefore the formation of O_2 molecule would involve sharing of two electrons from each oxygen atom. As sharing involving one electron pair is indicated by a single short straight line, the sharing of two electron pairs would be indicated by two short straight lines:



$$\cdot\ddot{\underset{\cdot\cdot}{O}}\cdot + \cdot\ddot{\underset{\cdot\cdot}{O}}\cdot \rightarrow \ddot{\underset{\cdot\cdot}{O}}::\ddot{\underset{\cdot\cdot}{O}} \quad \text{or} \quad \ddot{\underset{\cdot\cdot}{O}}=\ddot{\underset{\cdot\cdot}{O}}$$

Nitrogen atom, on the other hand, has five electrons in the valence shell, therefore, the formation of N_2 molecule would involve sharing of three electrons from each of the two atoms as shown below. A triple bond as in N_2 is represented by three short lines.



$$\cdot\ddot{\underset{\cdot}{N}}\cdot + \cdot\ddot{\underset{\cdot}{N}}\cdot \rightarrow \ddot{N}\vdots\vdots\ddot{N} \quad \text{or} \quad \ddot{N}\equiv\ddot{N}$$

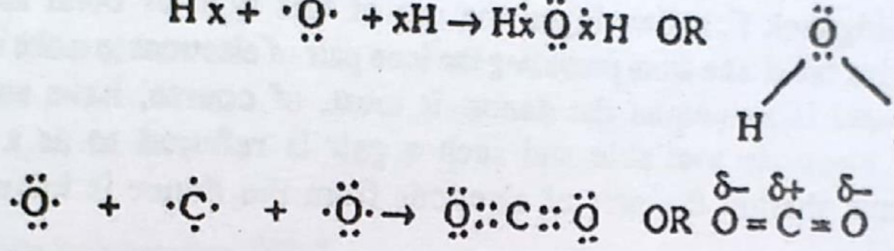
The bond distances of multiple bonds are shorter and the bond energies are higher as shown in the table 4.1 (Also refer 4.7).

Table 4.1 Bond distances and Bond Energies of Single, Double, Triple bonds.

Covalent Bond	Bond Distance	Bond Energy
C – C	1.54A	347 KJ mol^{-1}
C = C	1.34A	598 KJ mol^{-1}
C ≡ C	1.20A	820 KJ mol^{-1}
Cl – Cl	1.99A	242 KJ mol^{-1}
O = O	1.21A	498 KJ mol^{-1}
N ≡ N	1.10A	946 KJ mol^{-1}

Generally there is shortening of 0.20Å for any double bond and 0.34 Å shortening for any triple bond.

Notice that the examples given so far involve the equal sharing of electrons between similar atoms which form pure covalent bonds. Examples of bonding in water and CO_2 present an interesting situation, where sharing of electrons takes place between dissimilar atoms.



$$H\times + \cdot\ddot{\underset{..}{O}}\cdot + \times H \rightarrow H\overset{\cdot}{\times}\ddot{\underset{..}{O}}\overset{\cdot}{\times}H \quad \text{OR}$$

$$\cdot\ddot{\underset{..}{O}}\cdot + \cdot\dot{\underset{\cdot}{C}}\cdot + \cdot\ddot{\underset{..}{O}}\cdot \rightarrow \ddot{\underset{..}{O}}::C::\ddot{\underset{..}{O}} \quad \text{OR} \quad \overset{\delta-}{O}=\overset{\delta+}{C}=\overset{\delta-}{O}$$

The shared electrons are attracted more towards more electro negative atom (Oxygen in both cases). Such a pair of electrons constitute *polar bond* making one part of a molecule partially negative (δ–) and the other partially positive (δ +). A molecule with a positive and negative pole is referred to as *dipole*. A covalent bond is directed in space so that the atoms in a covalent compound are linked in a definite position in relation to each other and the molecules formed may exist as distinct particles.

Characteristics of Covalent Compounds

(i) Unlike ionic compounds, the covalent compounds exist as separate covalent molecules, because the particles are electrically neutral and have little attractive forces for each other.

(ii) Covalent compounds, since they exist as separate molecules are expected to be volatile liquids or gases or low melting solids (held together by weak Vander Waals forces).

(iii) These are non-electrolytes i.e. they do not conduct electricity.

(iv) Covalent compounds are generally insoluble in water and similar polar solvent but soluble in the organic solvents.

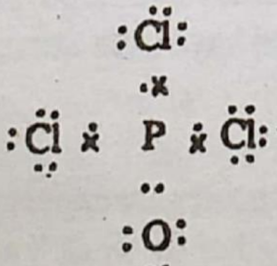
4.4 CO-ORDINATE OR DATIVE COVALENT BOND

An atom in groups VA, VIA or VIIA, having filled its valence shell by sharing its unpaired electrons to form covalent bonds, may use its remaining paired electrons (lone pairs) to form further bonds. It does this by sharing a pair with another atom having an empty orbital. The result is a dative or co-ordinate bond in which both electrons in the shared pair originate from the same atom. Sidgwick first developed the use of this type of bond and he called it as dative bond. The atom providing the lone pair of electrons to make up the co-ordinate bond is known as the donor. It must, of course, have an 'un-used' pair of electrons available and such a pair is referred to as a lone pair. The atoms sharing the pair of electrons from the donor is known as the acceptor.

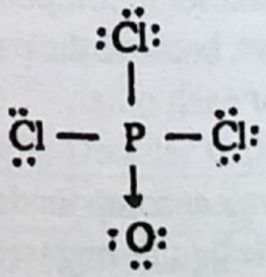
The dative bond is represented either by the use of an arrow, from the donor to the acceptor atom or by means of line, conveniently used to represent a covalent bond, but with inclusion of charges (+) for the donor and (-) for the acceptor atom. On this basis, the dative bond can be regarded as a covanlent bond with a certain amount of ionic character, and the term co-ionic instead of dative, is intended to describe this state of affairs.

EXAMPLES

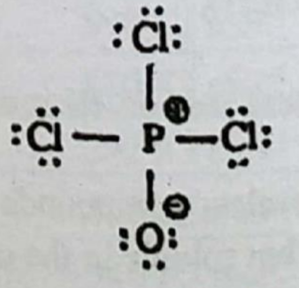
(i). Phosphorus Oxychloride, $POCl_3$.



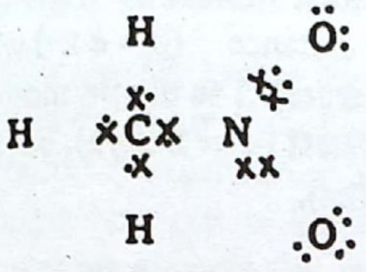
which may be represented as



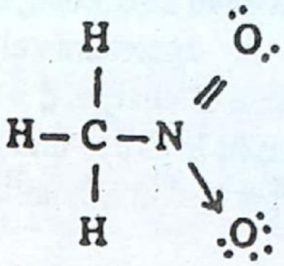
or as



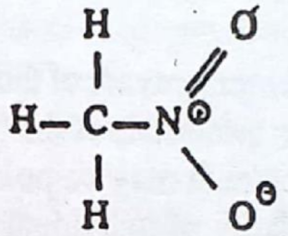
(ii) Nitro methane, $CH_3 NO_2$



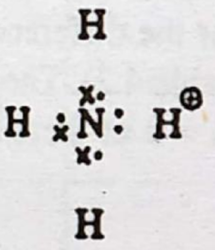
or



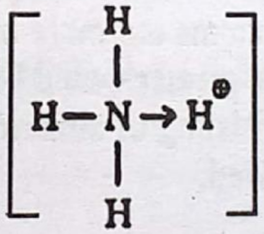
or



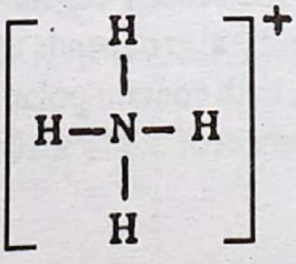
(iii) Ammonium ion, $\dot{N}H_4^+$



or



or



It may be pointed out that the co-ordinate bond and a covalent bond once formed are indistinguishable i.e. both are alike.

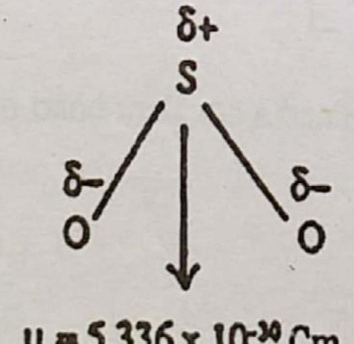
4.5 DIPOLE MOMENT

A magnet has the magnetic moment ml, where m = polar strength and l = distance between the two poles. A magnet tends to become oriented in a magnetic field. Likewise a dipole (polar molecule)-tends to become oriented in an electrical field. The extent of this tendency is referred to as the *dipole moment*, μ. It is measured by the magnitude of charge at each pole multiplied by the distance between two charges. The separation which in case of a diatomic molecule is approximately equal to the bond distance ($\mu = e \times d$ where e = magnitude of charge, d = distance between charges). The dipole moments were expressed in debye units (after the Dutch physicst Peter Debye), but now they are expressed in S.I. units as coulomb metre (Cm).

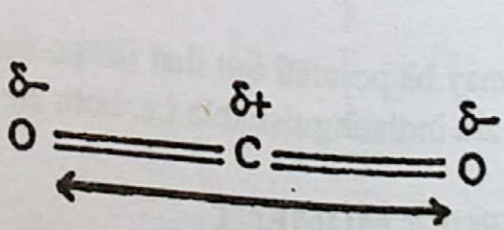
$$1 \text{ debye} = 10^{-18} \text{ esu} \times \text{cm} = 3.335 \times 10^{-30} \text{ Cm} \quad (1\text{C} = 2.998 \times 10^{9} \text{ esu})$$

The dipole moments are of the order of 10^{-30} Cm and it is due to the fact that the charge on an electron is of the order of 10^{-19} coulombs and distance is of the order of 10^{-10} metre. It may be pointed out that the dipole moment depends not only on the polarity of individual bond in a given molecule, but also on the geometry of a molecule as a whole. For diatomic molecule, polar bond means polar molecule, that is the two concepts coincide. The diatomic molecules consisting of different atoms are more or less polar. Greater the difference of electronegativity, Δ EN, greater would be the polarity (see table 4.2). The pure covalent molecules consisting of similar atoms will have $\mu = 0$ as there is no charge separation involved.

For polyatomic molecules, dipole moment not only depends upon the polarity of its bonds but it also depends upon the geometry of the molecule. SO_2 and CO_2, for instance, both contain polar bonds but the angular structure of SO_2 results in a dipole moment of 5.336×10^{-30} cm, while for linear CO_2, $\mu = 0$.



$\mu = 5.336 \times 10^{-30}$ Cm



$\mu = 0$

The net molecular moment is indicated by (→) and it is the vector sum of the individual bond moments. In CO_2, the double bonds lie on one straight line, that is, molecule is perfectly symmetrical. Hence although both bonds in CO_2 are polar, the two dipole moments of the molecule are equal oppositely directed, thus the molecule as a whole is nonpolar. Likewise CS_2 is also non polar ($\mu = O$)

Now consider carbon tetra chloride ($C\,Cl_4$) which contains four C – Cl bonds which are definitely polar but the symmetry gives $C\,Cl_4$ a zero dipole moment. Chloroform molecule ($CHCl_3$) on the other has a dipole moment of 3.40×10^{-30} cm due to its asymmetrical structure. Dipole moments of some molecules are given in the table 4.2.

Table 4.2 Dipole moments in debye and coulomb metre.

Molecule	μ = debye	μ = Cm	Molecule	μ = Debye	μ = Cm
(i) H_2	O	O	(vi) HCl	1.03	3.436×10^{-30}
(ii) Cl_2	O	O	(vii) H_2O	1.84	6.137×10^{-30}
(iii) CCl_4	O	O	(viii) NH_3	1.46	5.002×10^{-30}
(iv) CO_2	O	O	(ix) C_6H_6	O	O
(v) HF	1.90	6.369×10^{-30}	(x) $CHCl_3$	1.02	3.40×10^{-30}

4.6 IONIC CHARACTER OF COVALENT BOND

It was made clear in the previous section that in case of Cl_2, O_2 and N_2 molecules where the atoms are identical, the shared electrons are equally attracted due to identical electronegativities; neither atom attracts electrons more strongly than the other and the electron density is distributed equally over the two atoms in a molecule. Cl_2, O_2 and N_2 molecules are therefore *non-polar.*

The molecules consisting of different atoms such as H_2O, HF etc. present a different situation. In these cases, the shared electrons are not equally attracted. In H_2O, for instance, oxygen attracts the bonding electrons to a greater extent. The electron cloud of the molecule is shifted towards oxygen so that this end of molecule has a greater concentration of negative than positive charge. Similarly in HF molecule, fluorine is more electronegative, so this end has greater portion of the negative charge (Fig. 4.2). Consequently in both the molecules, H_2O and HF, the hydrogen end is correspondingly more positive. This situation is indicated by using the symbols δ and δ^+ when δ (delta) represents the partial electrostatic charge separated between the two atoms ($\delta^- + \delta^+ = 0$)

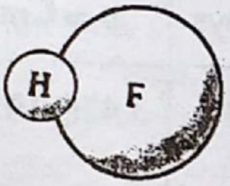
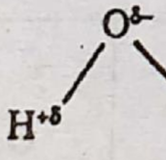


FIGURE 4.2
The electron density distribution in the HF molecule. The more electronegative fluorine atom attracts a large portion of the electron density cloud.



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

The covalent bonds in H_2O and HF are therefore *polarbonds*. These covalent bonds are not pure covalent but they have *partial ionic character*. The difference in the electronegativity of the two bonded atoms determines the extent of the ionic character of a covalent bond. For instance the H–F bond is 64% ionic and H–Cl is only 17% ionic. The partial ionic character greatly affects the properties of a molecule. For example, melting and boiling points of polar molecules are high and they are soluble in the polar solvent such as H_2O. Further more, the presence of partial character shortens the covalent bond, that is, pulls the atoms closer together. For example, the expected H–F bond distance is 1.01A where as the actual value is 0.92Å. Due to shortened bond distance it is quite obvious that the bond energy must increase accordingly. For example the bond energy of H–F molecule is 268 KJ/mol more than the calculated value.

4.7 BOND ENERGY

The energy change in chemical reactions is due to the bonds being formed and broken. A chemical bond is the link between two atoms and represents the lowering of energy. Work must be done if the atoms are to be separated. *The energy required to break a bond between two atoms in a diatomic molecule is known as the bond energy.* It is expressed in kilo joules per mole (i.e. the energy change per 6.02 x 10^{23} bonds):

$$\underset{\text{Hydrogen molecule}}{H-H_{(g)}} \rightarrow \underset{\text{Free atoms of Hydrogen}}{2H_{(g)}} \qquad \Delta H = 435 \text{ KJ mol}^{-1}$$

$$\underset{\text{Oxygen molecule}}{O=O_{(g)}} \rightarrow \underset{\text{Free atoms of oxygen}}{2\,O_{(g)}} \qquad \Delta H = \ 498 \text{ KJ mol}^{-1}{}_{(g)}$$

Alternatively, the bond energy might be taken as the energy released in forming a bond from the free atoms (not from the elements in their standard states):

$$H_{(g)} + \quad H_{(g)} \rightarrow H-H_{(g)} \qquad \Delta H = -435 \text{ KJ mol}^{-1}$$

$$O_{(g)} + \quad O_{(g)} \rightarrow O=O_{(g)} \qquad \Delta H = -498 \text{ KJ mol}^{-1}$$

Notice that the breaking of bonds is endothermic and making of bonds is exothermic process.

Bond energy is the measure of the strength of bonds. Generally, bond energies of polar bonds are greater than the pure covalent bonds (non polar):

$$\underset{\text{Non-polar molecule}}{Cl-Cl_{(g)}} \rightarrow 2\,Cl_{(g)} \qquad \Delta H = 244 \text{ KJ mol}^{-1}$$

$$\underset{\text{Polar molecule.}}{H^{\delta+} — Cl^{\delta-}{}_{(g)}} \rightarrow H^{+}{}_{(g)} + Cl^{-}{}_{(g)} \qquad \Delta H = \ 431 \text{ KJ mol}^{-1}$$

It is worth while to remember that the bond energy depends upon the partial ionic character of a covalent bond. Larger the ionic character greater the value of bond energy.

Polar molecules	$\overset{\delta^+}{H} - \overset{\delta^-}{F}$	$\overset{\delta^+}{H} - \overset{\delta^-}{Cl}$	$\overset{\delta^+}{H} - \overset{\delta^-}{Br}$	$\overset{\delta^+}{H} - \overset{\delta^-}{I}$
Bond energy (KJmol^{-1})	565	431	364	299

The value of bond energy also depends upon the *bond distance*. Shorter the bond distance, stronger the bond and greater would be the bond energy. For example triple bonds are usually shorter than the double bonds which in turn are shorter than the single bonds. Hence the bond energies for multiple bonds would generally be greater than those of single bonds (See table 4.3)

Table 4.3 Bond distances and Bond energies for single, double and triple bonds.

BOND	BOND DISTANCE (A)	BOND ENERGY (KJ mol^{-1})
$C-C$	1.54 A	347
$C=C$	1.34	598
$C\equiv C$	1.20	820
$N\equiv N$	1.10	946

Information of bond energy can help in understanding of chemical reactivity. For instance, bond energies of H_2 and O_2 are higher than for most diatomic molecules and are sufficiently high so that when their molecules collide with each other at room temperature, they simply rebound and no chemical reaction occurs.

4.8 SIGMA AND PI BONDS

In 1916, Lewis introduced the electron pair concept of a covalent bond.

However, it failed to account for the geometry and magnetic properties of molecules. In 1927, Heitler and London extended the Lewis theory and proposed *valence Bond Theory* (VBT) and in the early 1930's Hund, Huckle, Mulliken and others developed an alternative theory which is known as the Molecular Orbital Theory (MOT). According to both these theories, a covalent bond is formed by the overlap (fusion) of the atomic orbitals. Nevertheless, valence bond theory suggests that the bonding electrons occupy the *atomic orbitals* of the bonded atoms and molecular orbital theory assumes that the electrons occupy the *molecular orbitals* which belong to the molecule as a whole.

An essential difference between atomic orbital and molecular orbital is that an electron in the atomic orbital is influenced by one nucleus (mono centric) and in the molecular orbital, it is influenced by more than one nucleus (polycentric). According to the molecular orbital theory, linear combination of atomic orbitals (LCAO) gives two kinds of molecular orbitals. A molecular orbital with high electron density in the region between two nuclei having lower energy (greater stability) than either of the parent atomic orbitals from which molecular orbital is derived known as molecular bonding orbital. The other molecular orbital having higher energy with a nodel plane or of low electron density between the two nuclei, is less stable than either of the parent atomic orbitals from which it is derived, is known as antibonding molecular orbital. The energy difference of bonding and antibonding orbitals is shown by the energy diagram in Fig.4.4.

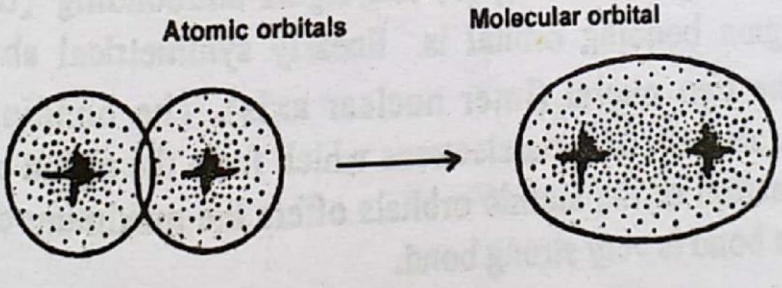


FIGURE 4.3
The two Is atomic orbitals and the resulting molecular orbital represented in terms of charge clouds.

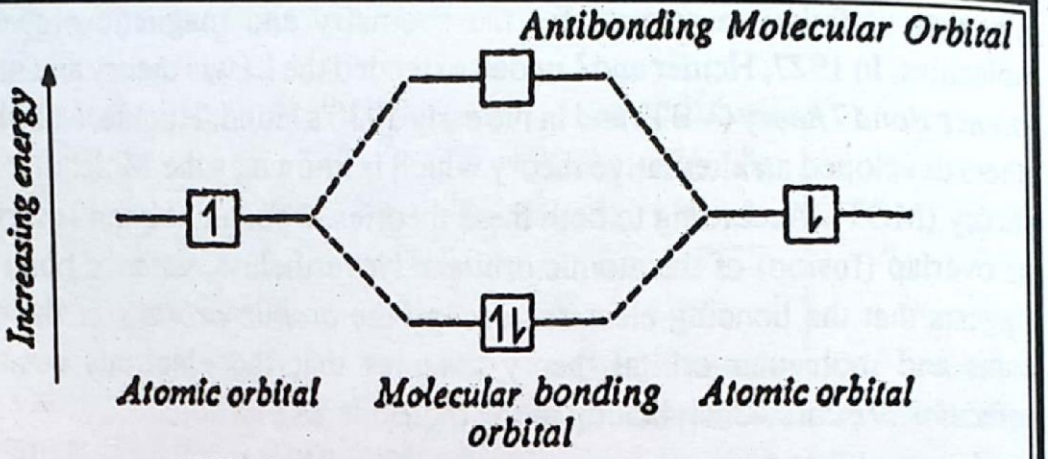


FIGURE 4.4
Energy diagram of bonding and anti bonding orbitals.

The bonding molecular orbitals which are formed by the linear combination or over lap of the two atomic orbitals, are designated by the Greek letter σ (sigma) and the bonding molecular orbitals which are formed by the parallel over lap of the two atomic orbitals, are designated by the Greek letter π (pi).

σ Bond: The 'linear' or 'head to head' overlap of the atomic orbitals like s - s, s - p, p - p give sigma bonding (σ) and sigma antibonding (σ^*) molecular orbitals. A sigma bonding orbital is linearly symmetrical about the axis connecting the two nuclei (inter nuclear axis). The bonding electrons contained in it are called sigma electrons which form the sigma bond. As the end on combination of the atomic orbitals offers the maximum overlape, the resulting sigma bond is very strong bond.

s-s type overlap is found in H_2 molecule when $1s^1$ orbital of one hydrogen overlaps $1s^1$ orbital of the other to form sigma bonding orbital which constitutes the single covalent bond in H_2 molecule. The antibonding orbital remains unoccupied (Fig: 4.5).

s-p type overlap occurs in HF molecule when $1s^1$ orbital of hydrogen overlaps 2 p orbital of fluorine to form sigma bonding orbital which constitutes the single covalent bond in HF molecule (Fig. 4.6)

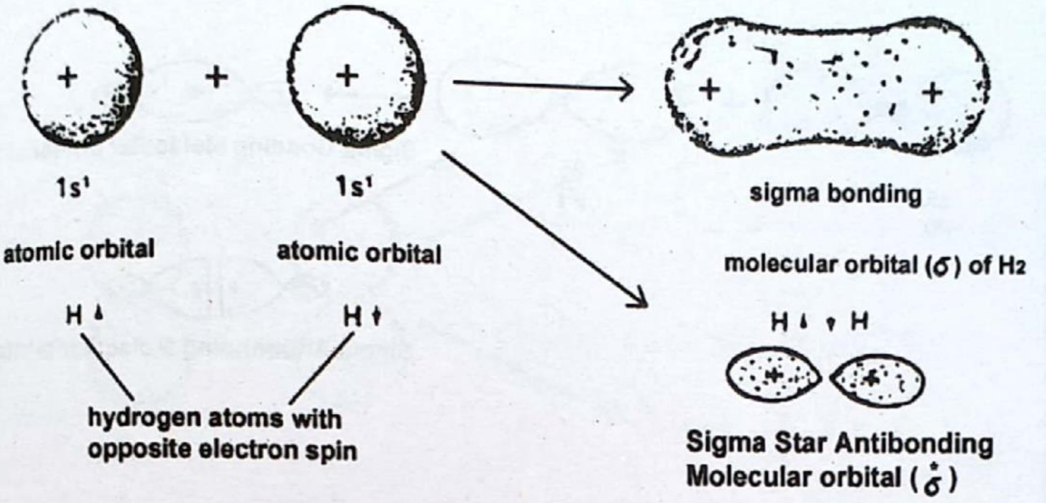


FIGURE 4.5
The hydrogen molecule.

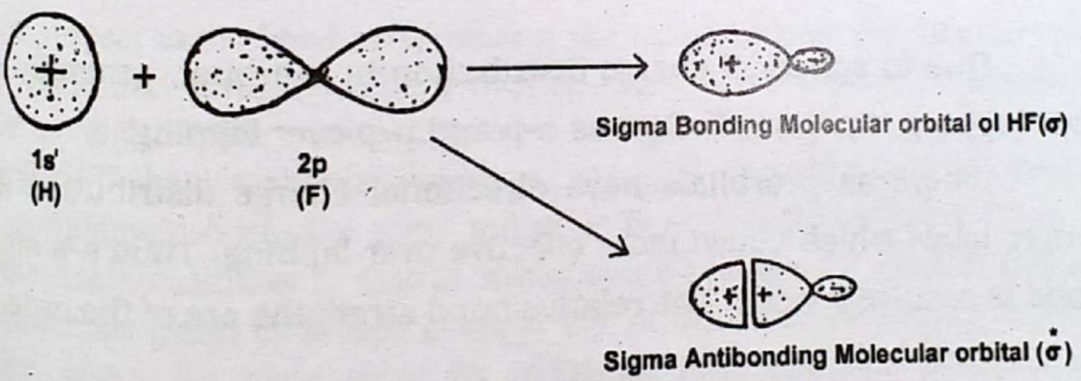


FIGURE 4.6
Hydrogen Fluoride molecule (HF)

p-p type overlap is seen in F_2 molecule where $2p_z$ orbital of one fluorine overlaps $2p_z$ orbital of the other fluorine to form F-F sigmabond. (fig. 4.7).

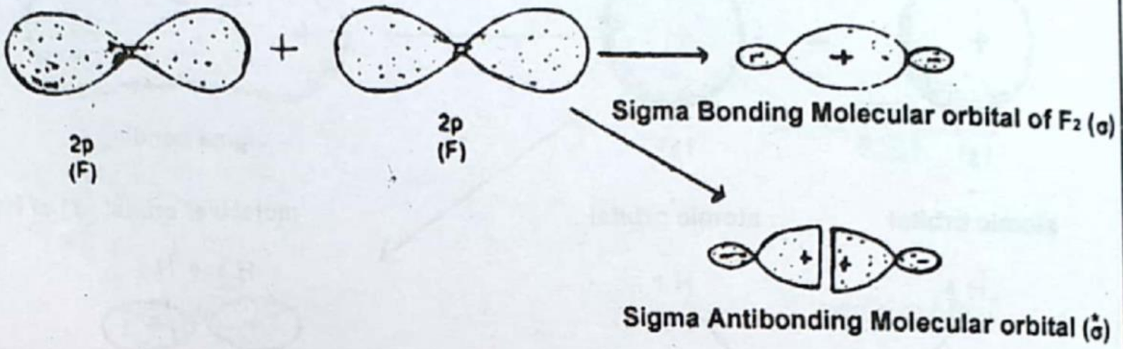


FIGURE 4.7
Flourine molecule (F_2)

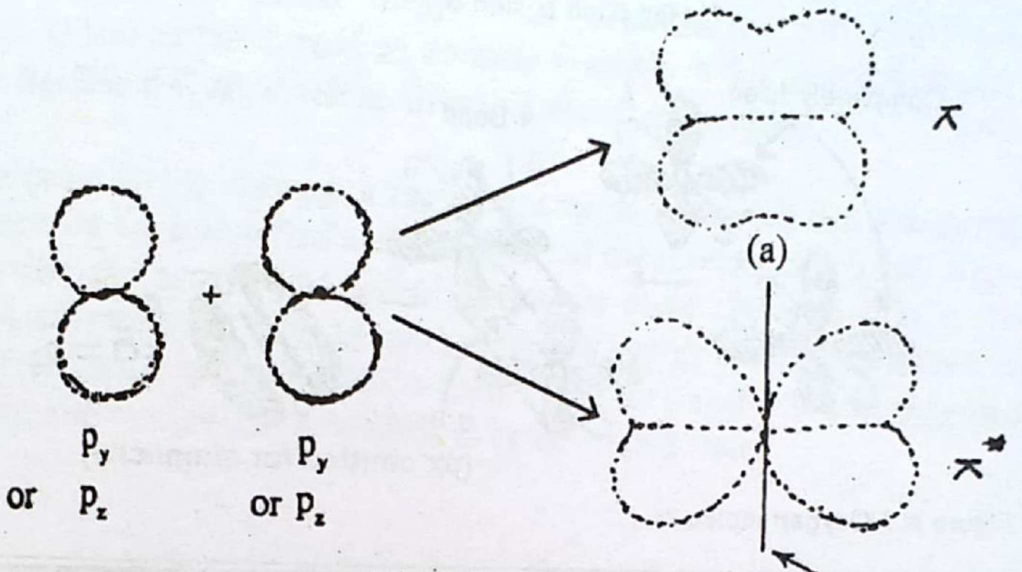
The relative strength of a sigma bond is related to the extent of overlap of the atomic orbitals. This is known as the *principle of maximum overlap*.

Due to spherical charge distribution in s–orbital, generally s–s over lapping is not so effective as s–p and p–p over lapping.

Where as p–orbitals have directional charge distribution and longer lobes which cause more effective over lapping. Thus s–s sigma bond is relatively weak. The relative bond strengths are of the order:

s − s,	s − p,	p − p
1.0	1.732	3.0

p$_i$ Bond: The 'lateral or side ways' overlap of the p-orbitals provided they are on the two atoms which are already bonded through a sigma bond and their axes are co-planar, gives two molecular orbitals – pi bonding (π) and pi antibonding (π*). The pi bonding orbital has two regions of electron density below and above the nodal plane (Fig. 4.8). The electrons contained in it are called pi bonding electrons which form the pi bond. It is not linearly symmetrical



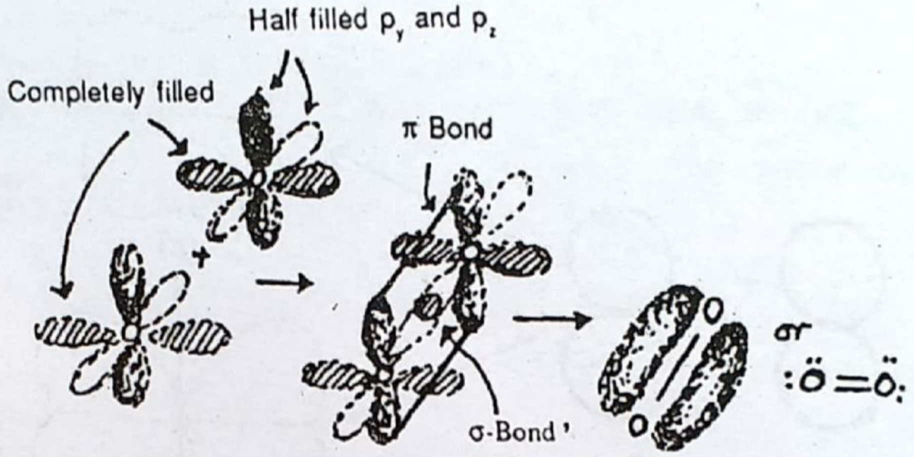
(a) π bonding (b)

(b) π^* Antibonding

FIGURE 4.8

with respect to the bond axis, rather it has a nodal plane; the rotation about the bond axis seriously affects overlap between the p-orbitals. Maximum overlap and therefore maximum bond strength requires two p orbital to be parallel. If the two atomic orbitals are mutually perpendicular, this overlap is at minimum (virtually zero) and there is essentially no bond. Thus the most stable condition is that in which two p-orbitals are parallel and this requires the atoms or groups at either end of the molecule should lie in the same plane, i.e. they must be coplanar. Any rotation of the atoms or groups at either end, with relative to one another requires sufficient energy to break the pi-bond. At room temperature, the molecules containing pi bond such as alkenes do not have sufficient energy to allow the rotation to take place, and the result is the restriction of rotation.

O_2 molecule is formed by the combination of two oxygen atoms. Each oxygen atom consists of two partially filled $2p_y$ and $2p_z$ orbitals. 2 p_y orbitals of the two atoms overlap end on to form a sigma bond leaving $2p_z$ orbitals parallel on the two atoms. The side to side overlap of $2p_z$ orbitals form a pi bond between the two oxygen atoms.



(px omitted for simplicity)

Figure 4.9 Oxygen molecule.

Fig: 4.9 Formation of sigma bond and pi bond between two oxygen atoms. Thus oxygen molecule consists of one sigma plus one pi bond (i.e. double bond). Similarly in nitrogen molecule, there is one sigma plus two pi bonds (i.e. triple bond).

From the above discussion we conclude that all the single bonds are sigma bonds, double bonds are one sigma plus one pi bond and the triple bonds are one sigma plus two pi bonds. Further more, a pi bond is weaker than sigma bond as the side ways overlap is less effective than the end on overlap.

4.9 HYBRIDIZATION

Valency is generally regarded as the number of unpaired electrons in the valence shell of an atom. However, this rule is disregarded in some cases such as Beryllium, Boron, Carbon etc. The electron arrangements of these elements in their ground states (low energy states) are given below:

		Is	2s	$2p_x$	$2p_y$	$2p_z$
$_4$Be	=	↑↓	↑↓			
$_5$B	=	↑↓	↑↓	↑		
$_6$C	=	↑↓	↑↓	↑	↑	

In terms of unpaired electrons beryllium would be expected to behave as an inert gas (valency = 0), boron might be expected to be mono valent (valency = 1) and carbon would be divalent (valency = 2). In actual practice, however, Be, B and C are divalent, trivalent and quadrivalent.

To account for the valency of such elements, it is assumed that some of the paired electrons are uncoupled and promoted to the orbitals of slightly higher energy within the same orbit before the atoms form chemical bonds. The promotion will require an input of energy but such energy will be available from the heat of reaction when additional covalent bonds are formed. The arrangement of electrons after promotion is referred to as an excited state.

		1s	2s	$2p_x$	$2p_y$	$2p_z$
Be*	=	⇅	↑	↑		
B*	=	⇅	↑	↑	↑	
C*	=	⇅	↑	↑	↑	↑

The asterisk denotes the excited state of the atoms. The excited structure for carbon would give three bonds involving p–orbitals which would be at right angles to each other together with a single bond involving an s-orbital. CH_4, for instance would be expected to contain three s–p bonds mutually at right angles, and one, weaker s-s bond. It is well established however, that the four bonds in CH_4 are all alike. Similarly in BCl_3, all the three B–Cl bonds are identical or equivalent.

To account for the equivalence of bonds, the concept of *hybrid orbitals* was introduced by *Linus Pauling*. He assumed that the atomic orbitals having nearly equal energies can be combined in various ways within an atom to form equivalent hybrid orbitals. The mixing of different atomic orbitals to produce the same number of equivalent orbitals, having same shape and energy is known as hybridization. The orbitals so formed are called hybrid orbitals and are designated according to the number of mixing orbitals.

Mixing Orbitals	No. and type of Hybrid orbitals produced.	Type of Hybridization
One s–and three p	Four sp^3 orbitals	sp^3
One s–and two p	Three sp^2 orbitals	sp^2
One s–and one p	Two sp^1 orbitals	sp^2

The case of carbon and its compounds is of great importance, for carbon forms such a wide variety of well known organic compounds. The various types of hybridization are therefore, discussed below with special reference to carbon compounds.

sp^3 (Tetra hedral) hybridization: Combination of one s– and three p– orbitals to produce four sp^3 hybrid orbitals is known as sp^3 or tetrahedral

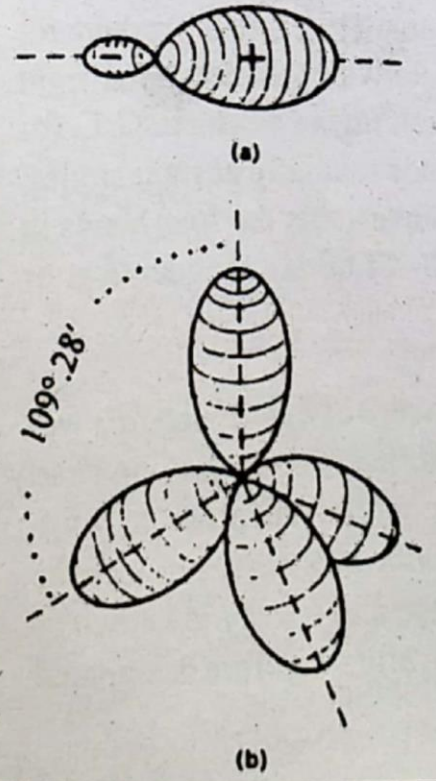


FIGURE 4.10
(a) A Sing sp^{3}hybrid orbital.
(b) Four tetrahedrally disposed sp^3 hybrid orbitals. (The smaller lobes are not shown).

hybridization. (Fig. 4.9). The hybrid orbitals are different than the pure s – or p– orbitals; they possess the character of both s– and p– orbitals in the ratio of 1:3. Sp^3 orbitals are directed towards the four corners of regular tetrahedron in which each angle is 109°. 28'. (Fig. 4.10). These orbitals can form stronger bonds than either s– or p– orbitals because of their size they can overlap more effectively. Sp^3 hybridization occurs in the saturated compounds in which the carbon is attached to four atoms. In methane, CH_4, for example Is– orbital of each hydrogen atom overalp with sp^3 hybrid orbital of the carbon atom to form four sigma bonds; the bond angle in CH_4 is 109°.28 (fig. 4.11). Other similar, symmetrical molecules involving sp^3 hybridization are CCl_4, $SiCl_4$, $SnCl_4$ etc. All such molecules have tetrahedral geometry like methane.

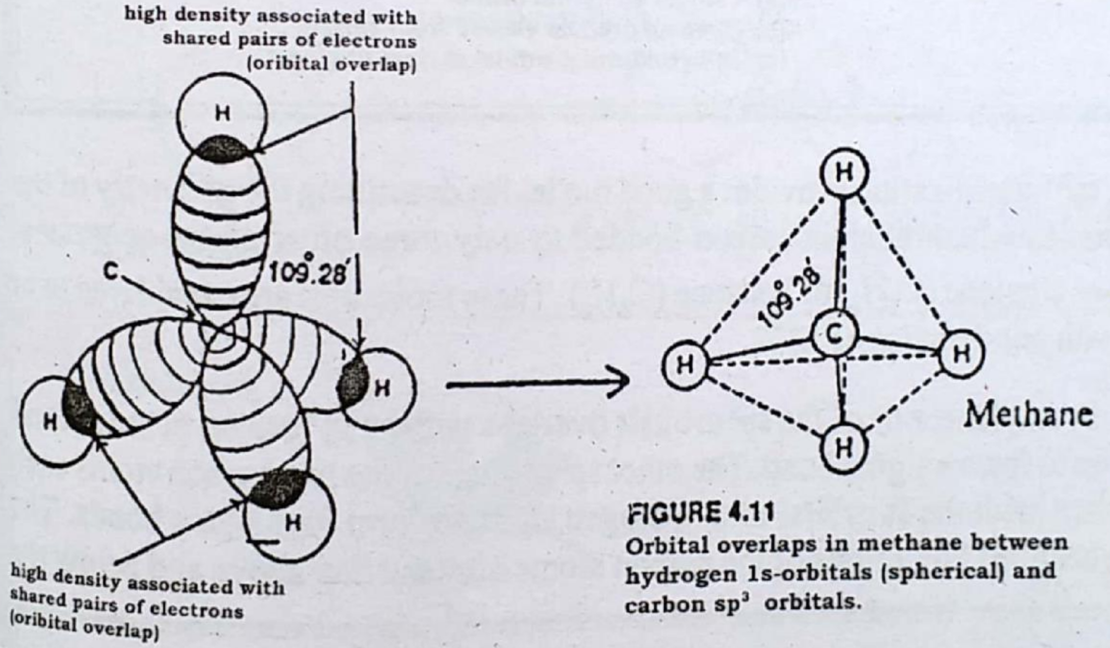


FIGURE 4.11
Orbital overlaps in methane between hydrogen 1s-orbitals (spherical) and carbon sp^3 orbitals.

sp^2 (Trigonal) hybridization: The mixing of one s- and two p- orbitals to produce three sp^2 hybrid orbitals is referred to as sp^2 or trigonal hybridization. These orbitals are co-planar and directed towards the corners of an equilateral triangle (trigonal) at angles of 120° to each other (fig. 4.12). sp^2 orbitals are different than either s – or p – orbitals and they are considered to have a character that is one third s and two thirds p. The fourth pure p – orbital which is not involved in hybridization remains unhybridized at right angles to the plane of the sp^2 orbitals (Fig. 4.12). Like sp^3 orbitals, the sp^2 orbitals can also form stronger bonds because on account of their size, they can overlap more effectively with the orbitals of the other atoms.

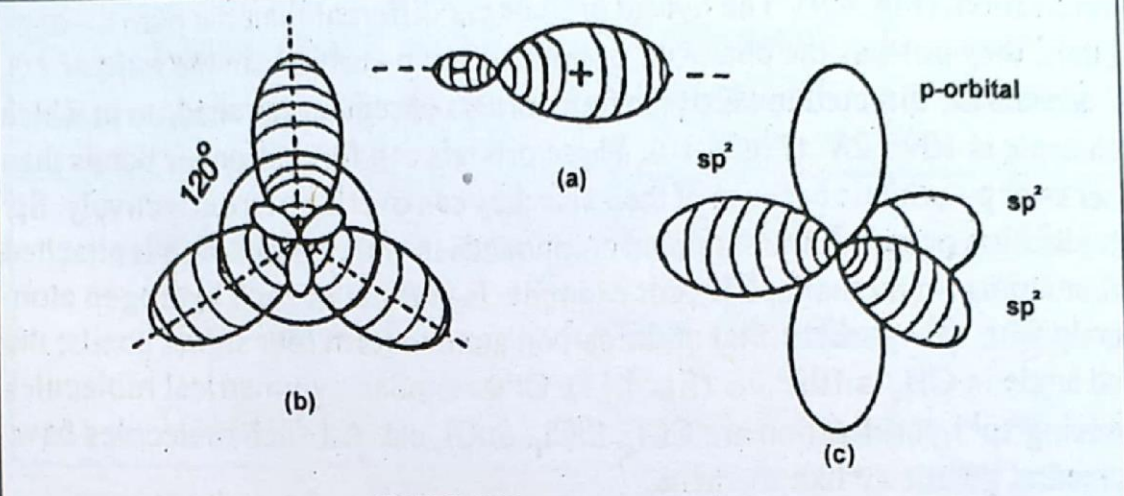


FIGURE 4.12
(a) A single sp^2 hybrid orbital
(b) Three sp^2 orbitals viewed from above
(c) Un-hybridized p-orbital at right angles

sp^2 hybridization provides a good model for describing the geometry of the molecules which contain carbon bonded to only three other atoms or groups, such as ethylene (C_2H_4) or benzene (C_6H_6). These molecules are considered to be flat with bond angles of 120°.

In ethylene, one of the sp^2 orbitals overlaps with an sp^2 orbital of the second carbon to form a sigma bond. The other sp^2 orbitals of the two carbon atoms each overlaps with the Is orbital of a hydrogen atom, to form four sigma bonds. The unhybridized 2p orbitals of the carbon atoms now overlap above and below the

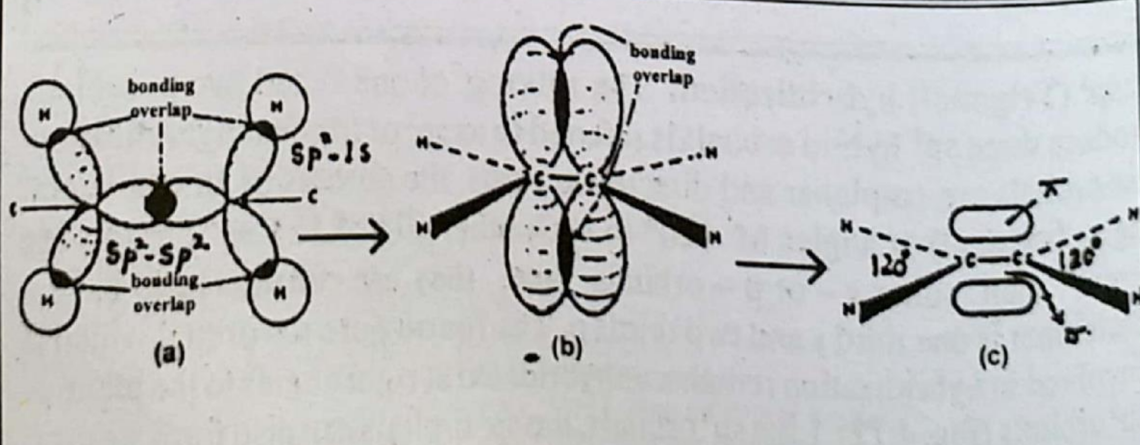
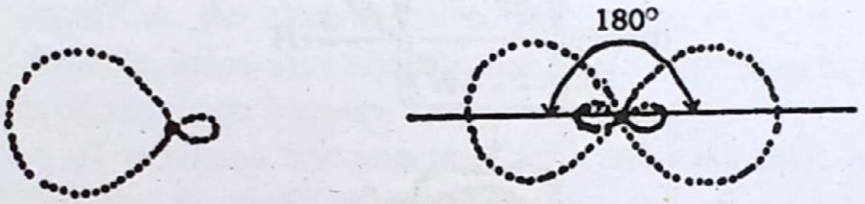


FIGURE 4.13
Molecular orbital diagram of Ethylene

plane to form a π bond (Fig. 4.13). Carbon-oxygen ($\rangle C = O$), carbon-nitrogen ($\rangle C = N-$) and other double bonds are formed in the same way. The two bonds (one sigma and one pi) making up the double bond are not equivalent to two single (sigma) bonds. It may be pointed out here that Boron also utilizes sp^2 orbitals for bond making (Section 4.9).

sp (diagonal) hybridization: The hybridization of an s- and a p- orbital leads to two hybrid orbitals known as sp orbitals. These orbitals are co-linear at an angle of 180° which provides maximum separation and overlap (Fig. 4.14). The unhybridized two p-orbitals ($2p_y$, $2p_z$) remain at right angles to the plane of the hybrid orbitals (Fig. 4.14).



(a) Single sp hybrid orbital:

(b) Two Co-linear sp hybrid orbitals

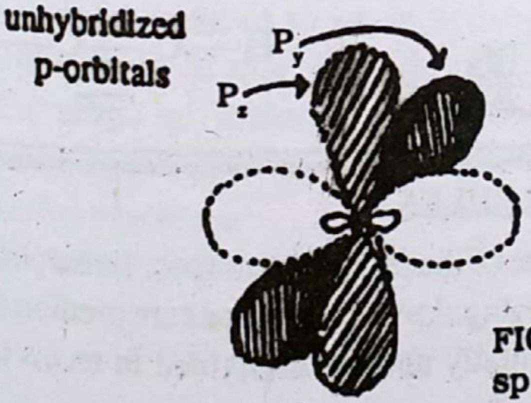


FIGURE 4.14
sp hybrid orbital with unhybridized P_y, P_z orbitals.

sp hybridization has been very useful in explaining the geometry of the molecules which contains carbon bonded to two other atoms or groups such as ethyne or acetylene (C_2H_2).

In ethyne molecule, one of the sp orbitals overlaps with one sp orbital of the second carbon to form a sigma bond, while the two remaining sp orbitals form sigma bonds with hydrogen atoms. The unhybridized p-orbitals overlap in parallel manner and two pi bonds are obtained in planes at right angles above below and on either side of the linear molecule (Fig. 4.15). like carbon, Beryllium utilizes sp^1 orbitals in bond making (Section 4.9).

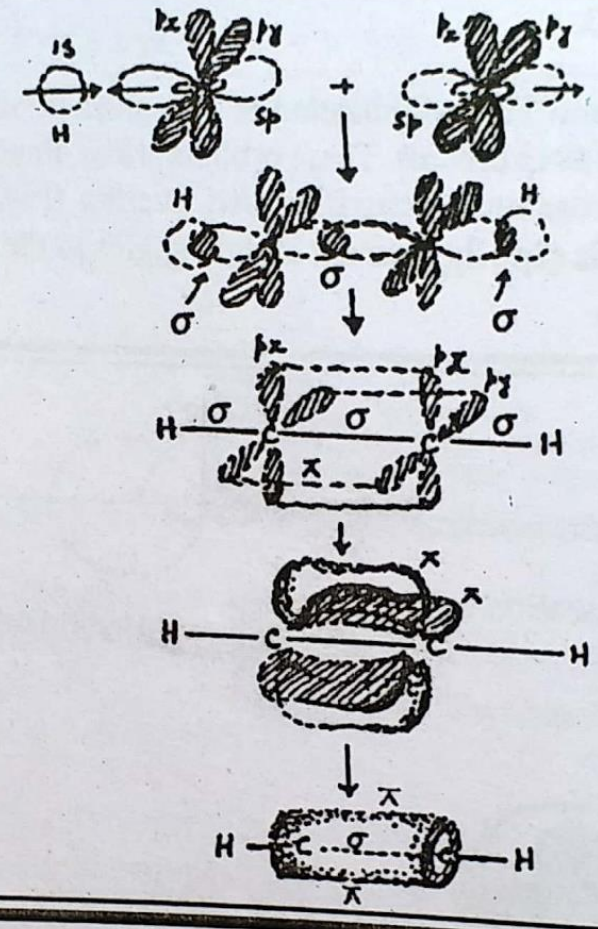


FIGURE 4.15
Bonding in Ethyne molecule

$$H\overset{\sigma}{—}C\,\overset{\pi}{\underset{\substack{\sigma\\ \pi}}{\equiv}}\,C\overset{\sigma}{—}H$$

4.10 SHAPE. OF SIMPLE MOLECULES

A simple molecule may acquire one of the following shapes: *linear, trigonal planar, tetra hedral, pyramidal, bent or angular*. These shapes are predicted from the bond angles determined experimentally and are explained in terms of two models:

(i) Electron pair repulsion model (ii). Hybrid orbital model.

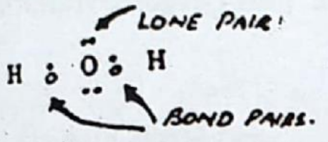
The assumptions of these models summarized below will serve as the guide lines to explain the shapes of molecules.

The electron pair repulsion model: This approach to the structure of a covalent molecule is due to SIGWICK and POWELL (1940).

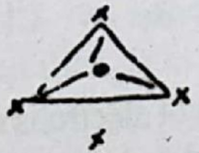
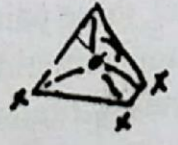
They pointed out that the shapes of molecules can be determined by the repulsion between the electron pairs present in valency shell of central atom.

The main postulates of this model or theory are:

1. There may be two types of electron pairs surrounding the central atom
   - (a) Bond Pairs : These are the result of the sharing of unpaired electrons of central atom with unpaired electrons of surrounding atoms. These are also called ACTIVE SET OF ELECTRONS.
   - (b) Lone Pairs : These are the paired electrons, which have not taken part in sharing. They are also called NON-BONDING PAIRS. They are also considered to be ACTIVE SET OF ELECTRONS.



2. Being similarly charged (i.e. negative) the bond pairs as well as the lone pairs repel each other.
3. Due to repulsion, the electron pairs of central atom try to be as far apart as possible, hence they orient themselves in space in such a manner that force of repulsion between them is minimized.
4. The force of repulsion between lone pairs and bond pairs is not the same. The order of repulsion is as follows:
   Lone pair — Lone pair repulsion > Lone pair — Bond pair repulsion > Bond pair — Bond pair repulsion.
5. In case of molecules with double and triple bonds, the π electron pairs are not considered to be an active set of electrons, hence not included in the count of total electron pairs.
6. The shape of molecule depends upon total number of electron pairs (bonding and lone pairs).It is summarized as follows.

Number of electron pairs around central atom		Geometry of Molecule	Bond Angle	Example
2	Linear		180°	$BeCl_2$; C_2H_2; CO_2; CS_2
3	Planar Trigonal		120°	BF_3; C_2H_4; SO_2; CO_3^{-2}
4	Tetrahedral		109°	CH_4; NH_3; H_2O CCl_4; CBr_4

Hybrid Orbital Model assumes that it is the nature of hybrid orbitals (i.e. hybridization) which determines the shape of a molecule.

sp-hybridization in the central atom gives linear molecule with an angle of 180°.

sp^2-hybridization in the central atom gives planar trigonal structure with an angle of 120°.

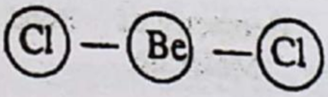
sp^3-hybridization with no lone pair or non-bonding orbital on the central atom gives tetrahedral geometry with bond angles of 109°. 28'.

sp^3-hybridization with one nonbonding orbital (lone pair) gives pyramidal structure with an angle of 107°.

sp^3-hybridization with two non-bonding orbital on central atom gives bent or angular structure with bond angle of 104.5°.

The larger atoms of Groups VA and VIA such as phosphorus and sulphur do not use sp^3 hybrid orbitals in bond making, instead they utilize their p-orbitals which are mutually at right angles. Such elements form compounds with bond angles of about 90°.

Linear Molecules : All the diatomic molecules such as HF, HCl etc. are linear regardless of the number of active electron pairs surrounding the central atom. It is because, there are only two atoms in a diatomic molecule. Molecules containing more than two atoms can also have the linear shapes, for example, Beryllium Chloride ($BeCl_2$) is a triatomic linear molecule with the bond angle 180°.



The Lewis structure of $BeCl_2$ is represented as :

$$:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Cl}}}\ \underset{\cdot}{\times}\ \ \mathrm{Be}\ \ \underset{\cdot}{\times}\ \underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Cl}}}\ :$$

Here there are two active sets of electrons surrounding the Beryllium atoms. In terms of electron repulsion model, these pairs must be arranged as far apart as possible, that is, the two chlorine atoms should be placed on the opposite side of beryllium which would give the linear structure of $BeCl_2$.

In terms of hybrid model, beryllium uses its sp-hybrid orbitals in bond making (i.e. beryllium is sp-hybridized).

Be = $1s^2$, $2s^2$ Excited $1s^2$, $2s^1$, $2p_x^1$ Hybridization Two sp^1 orbitals.

Both the sp^1 orbitals are arranged linearly at an angle of 180°. These orbitals overlap with $3p_x$ orbitals of the two chlorine atoms to form two sigma bonds, all the three atoms being in straight line (Fig. 4.16).

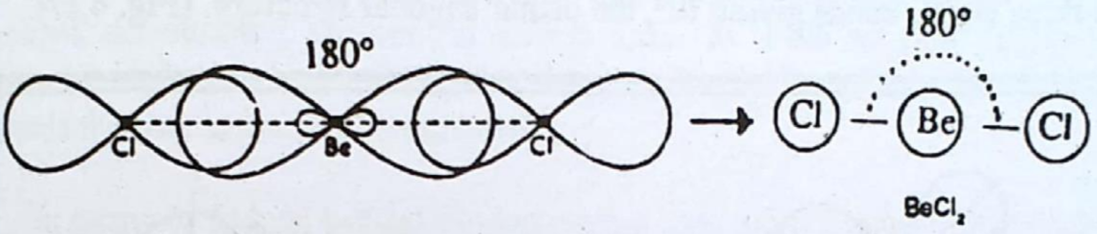


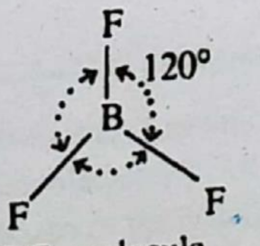
FIGURE 4.16
The formation of two a-bonds in $BeCl_2$ by overlap of $3p_x$ orbitals from two chlorine atom with two hybrid sp orbitals from a beryllium atom.

The linear structure of ethyne (H—C≡C—H) has already been discussed (Refer sp^1 hybridization). Likewise CO_2 and CS_2 are also linear molecules:

O = C = O　　　　S = C = S

(There are two electron pairs on the central atom carbon in each case)

Planar Trigonal Molecules : Boron trifluoride, BF_3, is a tetra-atomic planar trigonal molecule with the bond angles of 120°. The Lewis structure of BF_3 shows that there are three electron pairs surrounding the central Born atom. In terms of electron repulsion model, these electron pairs must be arranged as far apart as possible to minimize the repulsion, it is achieved by placing three fluorine atoms at the three corners of equilateral triangle in which each angle is of 120°.

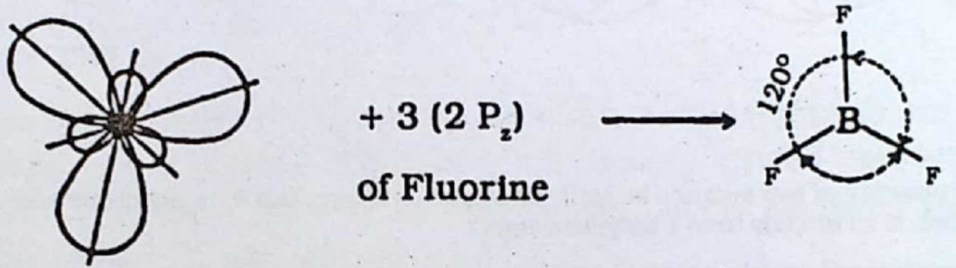


BF_3 molecule

In terms of the hybrid orbital model, boron atom undergoes sp^2 hybridization producing three sp^2 orbitals.

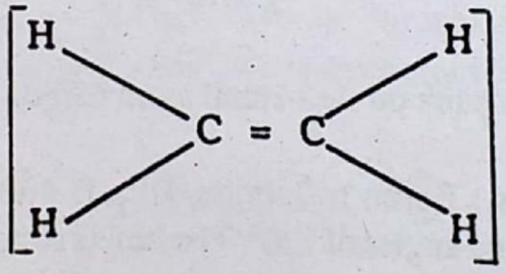
$B = 1s^2, 2s^2, 2p_x^1$ Excited $Is^2, 2s^1, 2p_x^1, 2p_y^1$ Hybridization Three sp^2 orbitals.

These orbitals are arranged trigonally in one plane (Coplanar) (Refer sp^2 hybridization). By overlapping with 2p orbitals of fluorine atoms, the sp^2 orbitals form three sigma bonds giving BF_3 the planar trigonal structure. (Fig. 4.17).

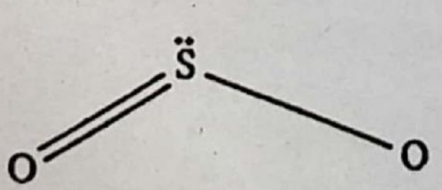


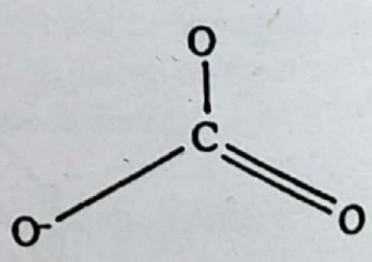
Three sp^2 orbitals of Boron.

FIGURE 4.17

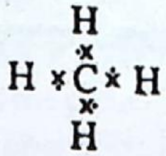


The planar trigonal geometry of Ethene has already been discussed in sp^2 hybridization. Sulphur dioxide, SO_2 and the carbonate ion, CO_3^{2-}, both have planar trigonal geometry because both S in SO_2 and C in CO_3^{2-} have three active sets of electrons surrounding them.





Tetrahedral Molecules : Methane, CH_4, is a tetrahedral molecule with bond angles 109°.28' (See Fig. 4.11) The Lewis structure of CH_4 is represented as :



$$\begin{array}{ccc} & H & \\ & \times & \\ H \times & C & \times H \\ & \times & \\ & H & \end{array}$$

In terms of electron pair repulsion model, there are four active sets of electrons surrounding the central carbon atom. In order to give maximum separation and minimum repulsion, the four hydrogen atoms must be directed towards the four corners of tetrahedron.

In terms of hybrid orbital model, carbon uses sp^3 orbitals to form sigma bonds with the hydrogen atoms as shown in the Fig. 4.18 (It has been discussed in sp^3 hybridization). Like wise all the compounds of CX_4 type such as CCl_4, CBr_4 etc. are tetrahedral with bond angles of 109°.28′

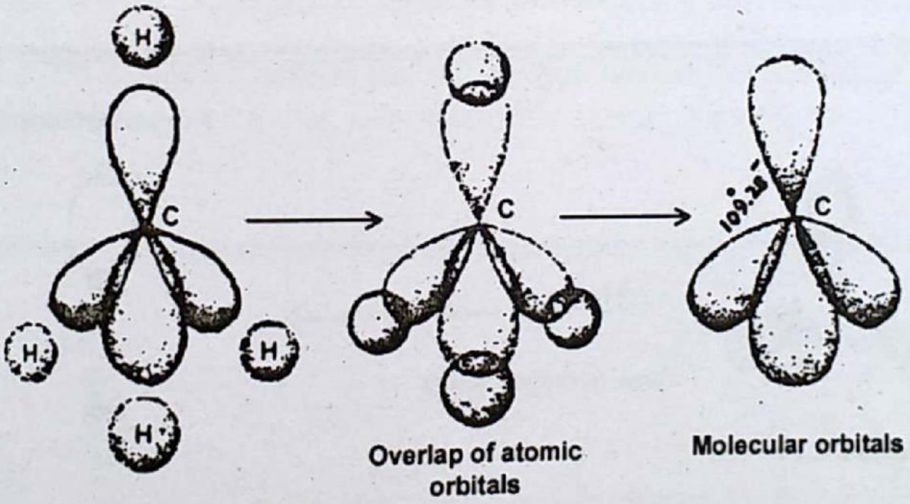


FIGURE 4.18
The structure of the methane molecule (the small lobes of the sp^3 orbitals have been omitted for simplicity).

Shape of Ammonia : The Lewis structure of NH_3 shows that the central atom nitrogen is surrounded by four electron pairs. In term of electron repulsions model, the tetrahedral structure gives the maximum separation as in the case of

CH_4. However, there is one lone pair electrons on nitrogen which repels the bonding pairs with the result that angle is reduced from 109° to 107°.

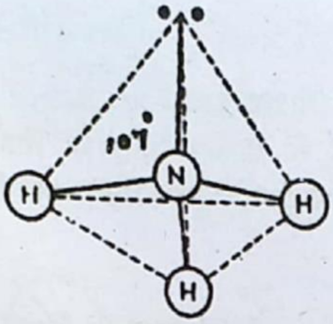


FIGURE 4.19
Shape of NH_3 molecule.

In term of hybrid orbital model, Nitrogen utilizes three of the four sp^3 orbitals to form sigma bonds with three hydrogen atoms having one non-bonding orbital on the nitrogen (Fig. 4.20). The deviation in the angle may be explained in terms of the non-bonding orbital.

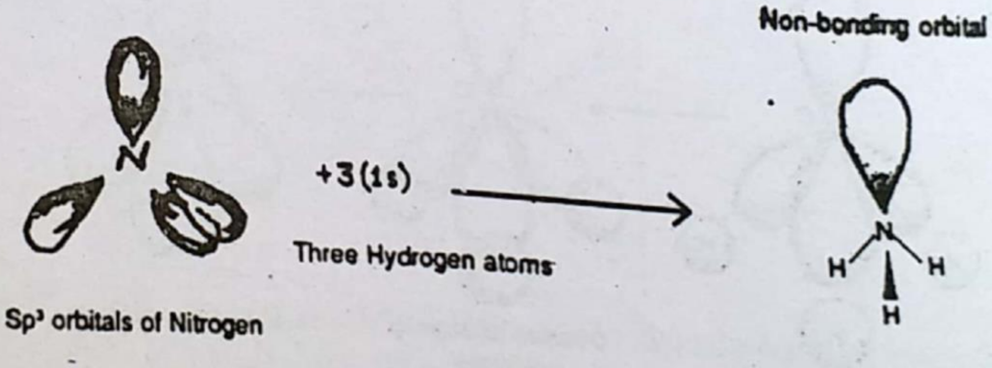


FIGURE 4.20
Shape of NH_3 molecule.

The electrons in the non-bonding orbital are associated with only one nucleus, and hence they are not held as tightly as the electrons in the bonding orbitals which are associated to two nuclei; consequently the non-bonding orbital occupies large volume of space. The larger orbital compresses the bonding orbitals slightly reducing the bond angle in the NH_3 to 107°

Shape of H_2O : As per Lewis Structure, the central atom oxygen is surrounded by the four active sets of electrons and according to the electron pair repulsion model, the tetrahedral arrangement would give maximum separation and minimum repulsion. However, the bond angle (H—O—H) is 104.5° (Fig. 4.21). The deviation in the angle is due to the presence of two lone pairs as explained in case of NH_3. The repulsion of the lone pairs and the bonded pairs reduces the angle from 109° to 104.5°.

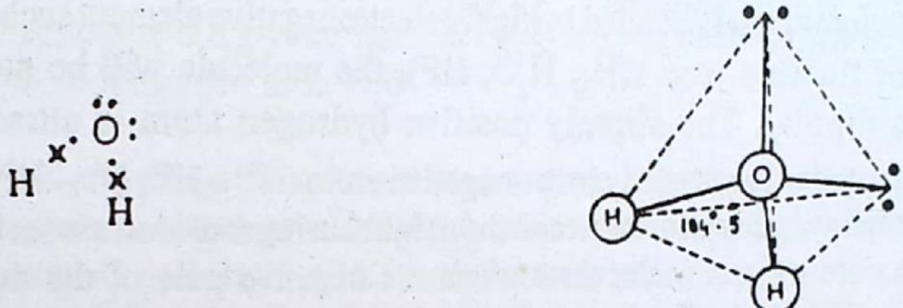


FIGURE 4.21
Shape of H_2O

In terms of hybrid orbital model, oxygen utilizes two of its sp^3 orbitals to form sigma bonds with the two hydrogen atoms, leaving two non-bonding orbitals on the oxygen.

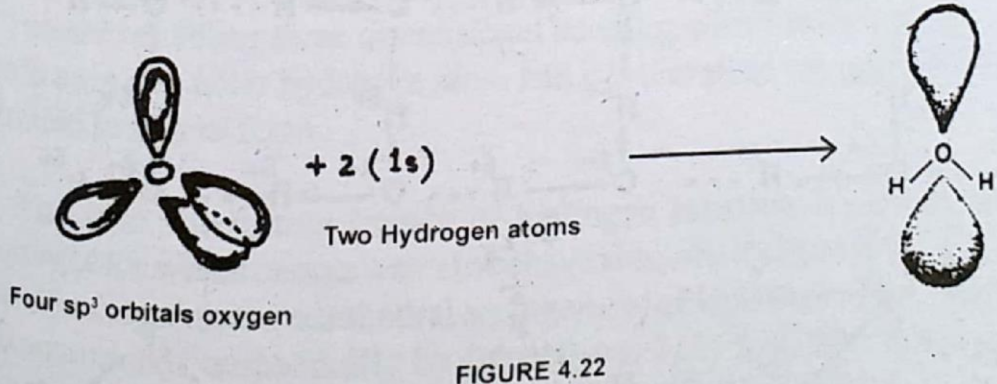


FIGURE 4.22
Shape of H_2O

As explained above, the non - bonding orbitals occupy the large volume of space, hence they compress the bonding orbitals and reduce the angle H–O–H in water to 104.5° giving angular or bent structure (Fig. 4.22).

Likewise, sulphur dichloride, SCl_2 is the angular molecule.

• 4.11 HYDROGEN BOND

Besides the ionic and covalent bonds which are the normal or primary bonds, there exists another type of bonding based on physical interaction of hydrogen atom called hydrogen bond.

When hydrogen is bonded to highly electronegative element such as nitrogen, oxygen or fluorine (e.g. NH_3, H_2O, HF), the molecule will be polarized and becomes dipolar. The slightly positive hydrogen atom is attracted by the slightly negatively charged electronegative atom ($N^{\delta-}-H^{\delta+}$, $O^{\delta-}-H^{\delta+}$, $F^{\delta-}-H^{\delta+}$). An electrostatic attraction between the neighbouring molecules is set up when the positive pole of one molecule attracts the negative pole of the neighbouring molecule. This type of attractive force which involves hydrogen is referred to as *hydrogen bond;* it is sometimes known as *protonic bridge.* To distinguish a hydrogen bond, it is best to write it as dotted line. The hydrogen bond causes the association of molecules as shown in fig. 4.23. Hydrogen fluoride and water, for instance are represented as $(HF)_x$ and $(H_2O)_x$.

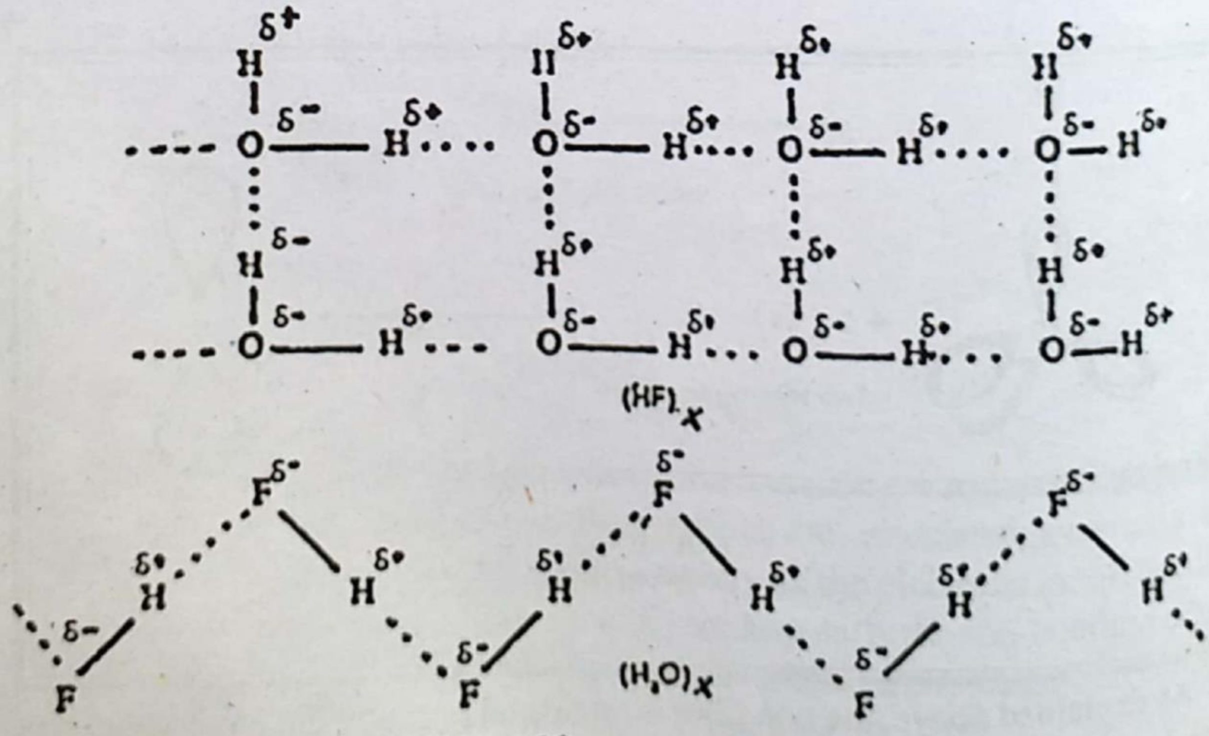


FIGURE 4.23
Association of HF and H_2O through hydrogen bonds.

Notice that within molecules, atoms are joined by strong covalent bonds but between the neighbouring molecules, hydrogen bonds exist. Thus hydrogen bonding is nothing but inter molecular attraction. The tendency to form hydrogen bonds increases rapidly from N–H through O–H to F–H and decreases from F–H to Cl–H and from O–H to S–H. Thus the tendency of a molecule to from hydrogen. bonds depends upon its ionic character which in turn depends upon the difference in electronegativity (ΔEN). Fluorine with the highest electronegativity forms the strongest hydrogen bonds. The bond strength (bond energy) of HF, H_2O and NH_3 (that is, for H......F, H......O and H......N) is 41.8, 29.4 and 8.4 KJ $mole^{-1}$ respectively. However the greater number of hydrogen bonds known are those which unite pairs of oxygen as in H_2O.

Although the hydrogen bonding is the strongest of the secondary bonds, it is still weaker than a normal covalent bond. It is evident from the fact that bond energy of hydrogen bonds is 20–40 KJ $mole^{-1}$ as compared to the bond energy of 150-500 KJ $mole^{-1}$ for normal covalent bonds.

The hydrogen bonding greatly affect the physical properties of molecules. For example, the first hydride in groups VA, VIA and VIIA of the periodic table (NH_3, H_2O and HF) have higher melting and boiling points than the other hydrides of these groups (e.g. PH_3, H_2S, HCl etc) as shown in the fig. 4.24.

Note that although fluorine is more electro negative than oxygen, water has a higher boiling point than hydrogen fluoride. This is because, the oxygen atom has two non-bonded pairs of electrons and there are two polar hydrogen atoms ($H^{\delta+}$) present enabling three dimensional bonding, where as in hydrogen fluoride, there is only one polar hydrogen atom and it is therefore only possible for chains of limited length to form.

The most interesting impact of hydrogen bonding is seen in the crystal structure of ice which causes water to behave abnormally from 0°C–4°C. Crystal structure of ice shows a tetrahedral arrangement of H_2O molecules. Each oxygen 'A' is surrounded tetrahedrally by four others, 1, 2, 3, 4. The hydrogen bonds shown by dotted lines (Fig. 4.25) link the pairs of oxygen atoms.

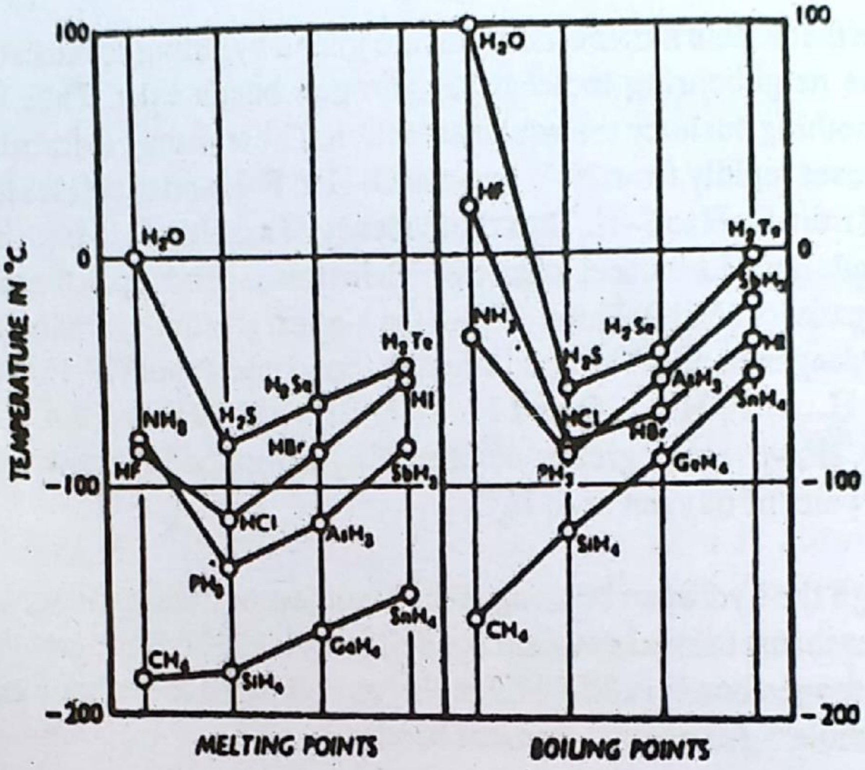


FIGURE 4.24
The abnormal melting and boiling points of water, hydrogen fluoride and ammonia.

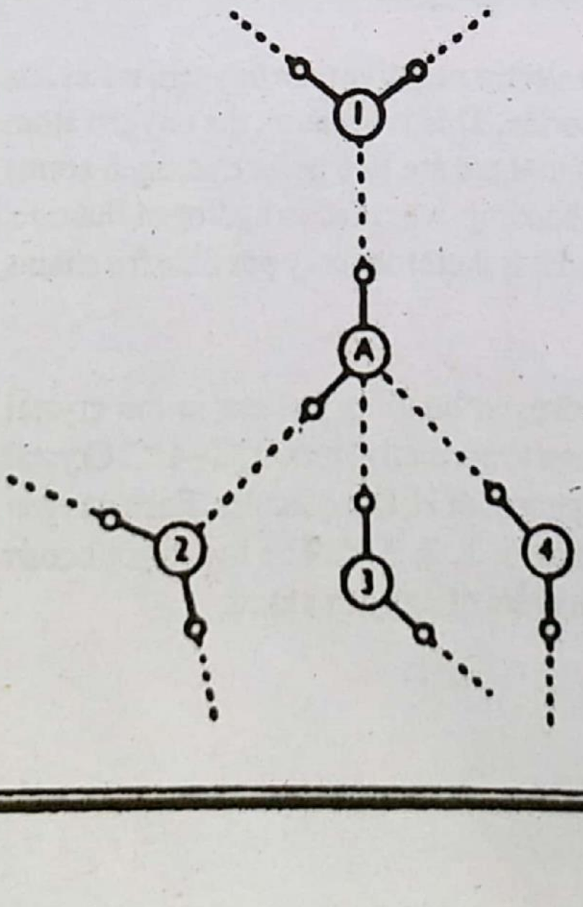


FIGURE 4.25
Crystal structure of ice.

The arrangement of the water molecules in ice is an open structure and due to larger volume, ice is less dense than liquid water. When ice melts some of the hydrogen bonds are broken and the molecules pack more closely together so that water has a higher density. This breaking down process is not complete until a temperature of 4°C is reached at which water has the maximum density. On these basis, the *anomalous* behaviour of water can be explained, that is, water when heated from o° to 4°C contracts and when cooled from 4°C to 0°C, water expands (contrary to the behaviour of other liquids).

PROGRESS TEST 4

1. Describe the main types of bonds. What physical properties are associated with the molecules containing these bonds.
2. What is polar colvalent bond? Do all polar molecules contain polar covalent bonds? Do polar covalent bonds necessarily have polarity on a polar molecule as a whole? Support your answer with more specific examples.
3. Distinguish between the following:
   (i) Atomic orbital and molecular orbital.
   (ii) Sigma and pi bonds.
   (iii) Valence Bonds theory and Molecular orbital theory.
4. What do you understand by the term Dipole moment? Explain the significance of dipole moment.
5. What is meant by sp^3 hybrid orbitals? How do they differ from s - and p - orbitals?
6. Describe how electronegativity of atoms can be used to predict the nature of bond formed between two elements. Explain giving examples.
7. Write note on Bond energy.
8. What are the most important secondary bonds present in H_2O and HF molecules? How do they affect the physical properties of compound?
9. How can the theory of electron pair repulsion be used to rationalize the shapes of simple molecules.
10. Beryllium chloride has a linear shape where as water molecule has angular shape. Account for this difference in terms of electron pair repulsion model and hybrid orbital model.
11. Predict the shapes of the following molecules:
    PCl_3, PH_3, H_2S, SCl_2.