

THE CHEMICAL BOND-II

17.1 INTRODUCTION

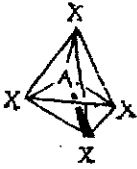


It has been recognized by chemists as long ago as the last century that atoms in molecules have definite arrangements in space, i.e., the molecules have well defined shapes or geometries. The properties of the molecules are strictly related to the shapes of molecules. This may be appreciated by recalling the differences in the properties of carbon allotropes-graphite and diamond, and red and white phosphorus. This point clearly illustrates the importance of geometric arrangement of atoms in molecules and chemists curiosity to unveil this information. In those days chemists had no direct method of determining the geometry of molecules. Only by studying the properties of materials, they were able to make intelligent deductions about the geometric arrangements of atoms in different molecules. However, we now have many direct methods. Different spectroscopic techniques such as infrared, Raman and nuclear magnetic resonance and single crystal X-ray diffraction method and electron diffraction data can give us exact information about bond distances and bond angles between various atoms in polyatomic molecules.

Lewis's concept of covalent bond formation gives us a good understanding about number of bonds formed by an atom in a covalent compound. Lewis structures give us information about the arrangement of electrons in molecules. The extension of this concept, which is discussed in this lesson, will help us in predicting the shapes (geometries) of molecules.

17.2 OBJECTIVES

After reading this lesson, you will be able to,

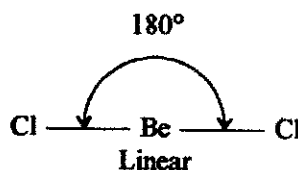
- state valence shell electron pair repulsion (VSEPR) theory,
 - list the various attributes of VSEPR theory upto six electron pairs only,
 - explain the hybridization of atomic orbitals with special reference to sp , sp^2 and sp^3 hybrid orbitals.
-

4	Tetrahedral	AX_4		$CH_4, CCl_4, NH_4^+, SiCl_4$
5	Trigonal bipyramid	AX_5		PCl_5, PF_5
6	Octahedral	AX_6		SF_6, PF_6^-

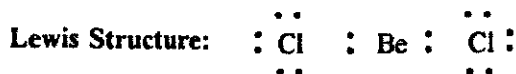
According to these postulates we may conclude that electron pairs behave as if they repel each other and attempt to keep as far away from each other as is possible.

17.3.1 VALENCE SHELL WITH BONDED PAIRS ONLY

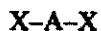
AX_2 Molecules: In $BeCl_2$, there two electron pairs in the valence shell of beryllium [Be has configuration $1s^2, 2s^2$, so it contributes two electrons to the valence shell and two more electrons (one from each chlorine atom) are contributed by two chlorine atoms]. Two electron pairs have a linear arrangement (Fig. 17.1)



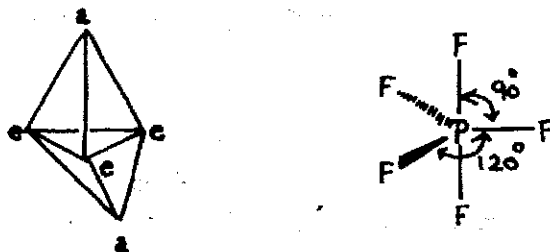
(Fig 17.1)



molecules (where A is the central atom and X are the atoms bonded to A) such as BeH_2 exhibit the same linear geometry.



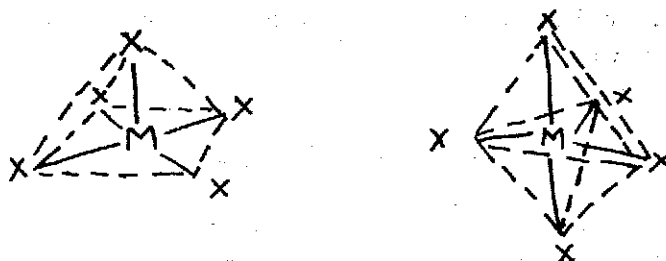
AX_3 Molecules: In BF_3 , there are three electron pairs in the valence shell of boron (B has electronic configuration $1s^2, 2s^2 2p^1$ and it thus contributes three electrons to the valence shell and three more electrons are contributed by three F atoms). Three electron pairs have



(Fig. 17.4)

The trigonal bipyramid has six equivalent triangular faces, nine edges and five vertices. Other molecules like PCl_5 , AsF_5 have this geometry. The angle between two equatorial bonds is 120° . The two axial bonds are usually slightly longer than the three equatorial bonds, because the axial positions, which have three nearest neighbours at 90° are more crowded than the equatorial positions, which have only two nearest neighbours at 90° . The axial atoms are therefore forced further away from the central atom than the equatorial atoms.

For five pairs, two structures namely square pyramid and trigonal bipyramid maximize the least distances between five pairs and are thus to be equally preferred. However, if we consider the number of least distances is also minimized, the trigonal bipyramid is to be the preferred arrangement. The number of least distances is smaller (six only) in trigonal bipyramid arrangement than in square pyramid geometry which has eight.



AX_6 Molecules: Sulphur hexafluoride, SF_6 has six pairs of electrons in the valence shell of sulphur atom (six electrons are contributed by sulphur and six electrons by six fluorine atoms). The arrangement that keeps six electron pairs as far apart as possible is octahedral as shown in (Fig. 17.5). An octahedron has eight equilateral triangular faces, twelve edges and six equivalent vertices. This is the only arrangement which maximizes the least distances between six pairs of electrons.

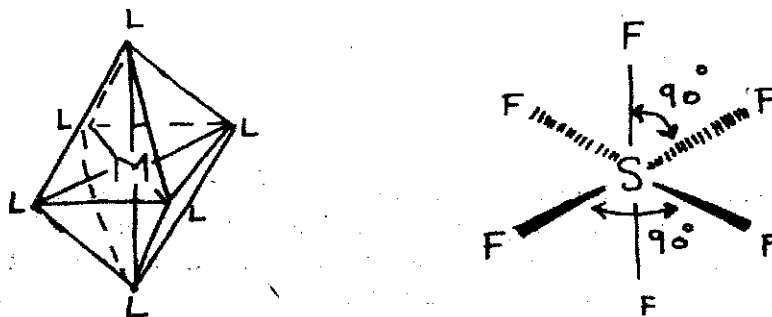


Fig 17.5

17.3.2 VALENCE SHELL WITH BONDED AND NON-BONDED (LONE) PAIRS

So far in this lesson we have considered only those shapes of molecules in which the central atom is bound by electron pair bonds. Considerable changes in the shapes take place when lone pairs of electrons are also present along with bond pairs in the valence shell of the central atom. We are now guided by a new assumption of VSEPR model:

IT IS ASSUMED THAT LONE PAIR OCCUPIES MORE SPACE IN THE VALENCE SHELL OF THE CENTRAL ATOM THAN THE BOND PAIR. (Postulate : 3)

This is a reasonable assumption because a lone pair on the central atom 'A' is only under the influence of the nuclear charge of A while the bond pair experiences the nuclear charges of two atoms A and X. The greater the charge experienced by the electron pair, the smaller the volume of the electron pair cloud. Therefore, a bonding pair which is associated with two nuclei would occupy less volume than a lone pair. Consequently, the order of repulsion would be:

lone pair-lone pair > lone pair-bond pair > bond pair-bond pair

Due to this reason, bond angles also deviate from regular geometry when lone pairs are present. Some examples are:

AX₂L Molecules: Tin (II) chloride (SnCl₂) is a typical example of this class of compounds which represent two bond pairs and one lone pair. Element tin belongs to Group 14 and therefore SnCl₂ has six electrons in the valence shell (4 electrons belong to tin atom and two electrons (one each) from two chlorine atoms). The three pairs should acquire an equilateral triangular arrangement (Bond angle = 120°).

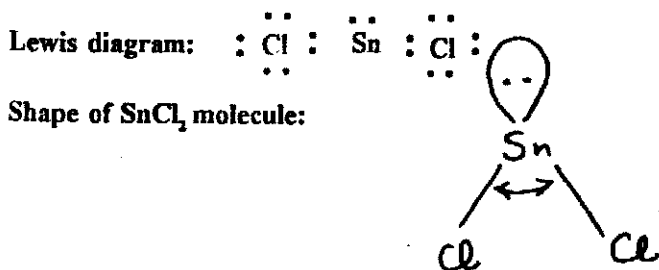
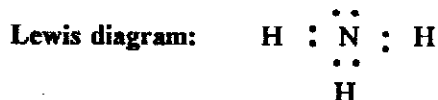


Fig. 17.6

Since one of the vertices of the triangle is occupied by a lone pair, therefore, the two bond pairs acquire an angular arrangement (Fig 17.6) The lone pair occupies more space and thus forces the two bond pairs to squeeze in lesser volume. Consequently, ClSnCl bond angle is slightly less than 120°.

AX₃L Molecules: Ammonia (NH₃) is a typical example of this class of compounds. The central nitrogen atom has four electron pairs (five electrons contributed by nitrogen and three (one each) by three hydrogen atoms). Out of the four electron pairs, three are bond pairs and one is a lone pair. Therefore one of the four vertices of the tetrahedron is occupied by a lone pair.



Shape of NH_3 molecule:

Because of greater lone pair-bond pair repulsions than bond pair-bond pair repulsions, the HNH bond angle is less than 109.5° (Fig 17.7). Some other examples of this type are PH_3 , PCl_3 , etc.

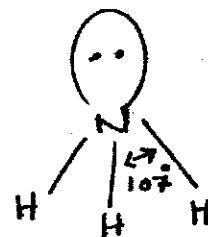


Fig. 17.7

AX_2L_2 Molecules: Water (H_2O) is an example of this class of compounds. The central oxygen atom has four electron pairs (six electrons contributed by oxygen atom and two electrons (one by each) by two H atoms) in its valence shell. The Lewis diagram shows that oxygen atom has two bond pairs and two lone pairs.



Shape of H_2O molecule:

Vertices of a tetrahedron are occupied by lone pairs (Fig 17.8) Such an arrangement gives angular shape to the molecule. Because of the presence of two lone pairs the bond angle shows an increased deviation from the tetrahedral angle than for AX_2L molecules which have only one lone pair. Other examples of this type include F_2O , SF_2 , SCl_2 , H_2S etc.

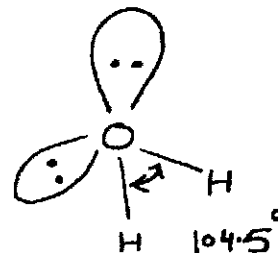
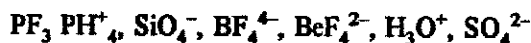


Fig. 17.8

INTEXT QUESTIONS 17.1

1. Classify the following molecules and ions as AX_n , AX_2L_2 and define their shapes



2. What are the shapes of the following molecules/ions ?



3. Using VSEPR theory, justify that HNH angle in NH_3 is less than 109.5° .

.....

17.4 HYBRIDIZATION OF ATOMIC ORBITALS

If we have to describe the bonding orbitals for the formation of H_2O molecule — we can use the two singly occupied $2p$ orbitals of an oxygen atom (electronic configuration of oxygen is $1s^2, 2s^2 2p^4$) to form localized bonding orbitals by combining them with $1s$ atomic orbital of H atom. The two $2p$ orbitals are at 90° to each other. It suggests that the HOH angle in H_2O molecule should be 90° . However, the observed HOH bond angle in water is 104.5° . Therefore the use of pure $2p$ atomic orbitals to explain the nature of bonding orbitals involved in the formation of H_2O molecule is not satisfactory.

The mixing of orbitals is called hybridization.

17.4.1 AX_2 MOLECULES: sp Hybridization.

In order to understand the concept of hybridization, we may first consider the linear BeH_2 molecule. The ground state electronic configuration of Be atom is: $1s^2, 2s^2$.

The excited state electronic configuration of Be is $1s^2, 2s^1, 2p^1$.

By the combination of $2s$ and $2p$ atomic orbitals, we may obtain two new *equivalent sp hybrid orbitals* which are at 180° with respect to each other.



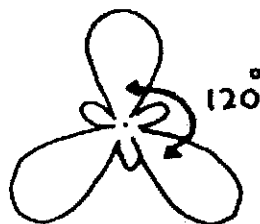
Fig. 17.9

The concept of hybridization can be rationalized on the basis that just like s , p and d set of orbitals are used to describe polyelectronic atoms, we can as well use combination of these orbitals for the description of electrons in a polyelectronic molecule. It should be noted that hybridization is not a physical process but a mathematical operation by means of which a set of atomic orbital is converted into an equivalent set of hybrid orbitals. Some other points about hybridization are:

1. A set of hybrid orbitals gives the same electron density distribution for the atom as the set of atomic orbitals from which it is obtained.
2. Hybrid orbitals are more directional and therefore are more effective in forming strong bonds due to better overlap.

17.4.2 AX_3 Molecules: sp^3 HYBRIDIZATION

In order to understand the bonding orbitals involved in the triangular planar molecule BF_3 , we may combine one $2s$ orbital and two $2p$ orbitals of boron to form three equivalent sp^2 hybrid orbitals. These sp^2 hybrid orbitals have their lobes which have their maxima (swollen lobes indicating high electron density) pointing towards the corners of an equilateral triangle.

Three sp^2 hybrid orbitals

Each of these hybrid orbitals can overlap with a $2p$ orbital on a fluorine atom to form a bonding orbital (Fig. 17.10).

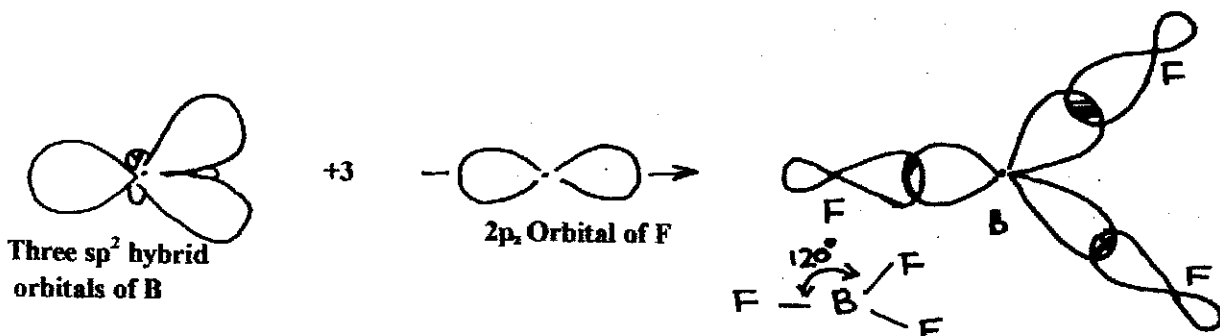


Fig 17.10: The formation of BF_3 , using sp^2 hybrid orbitals on boron and $2p$ atomic orbitals on fluorine atoms.

17.4.3 AX₄ MOLECULES: sp^3 HYBRIDIZATION

In order to explain the bonding in methane, we may construct four equivalent sp^3 hybrid orbitals by combination of one $2s$ and three $2p$ orbitals of carbon. The four sp^3 hybrid orbitals are directed toward the corners of a tetrahedron. Each of these hybrid orbitals can overlap with a $2s$ orbital on a hydrogen atom to form localized bonding orbitals (Fig. 17.11).

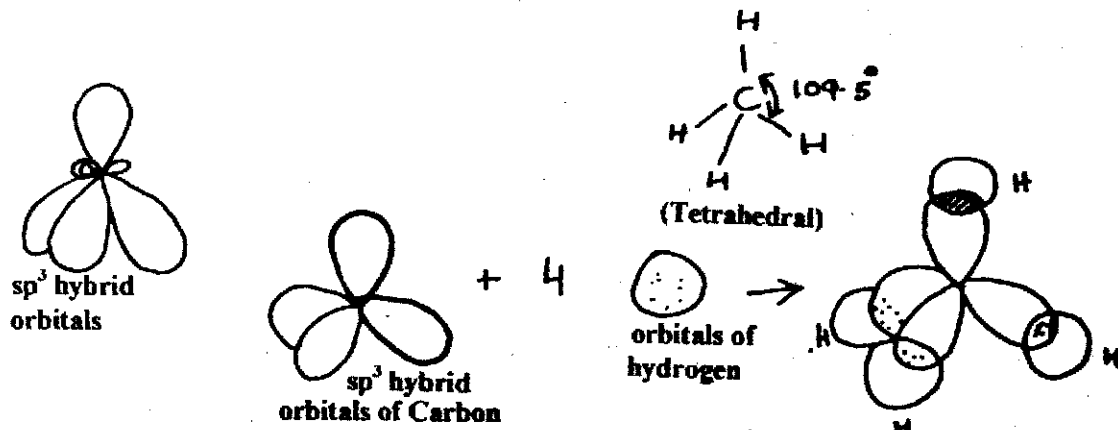
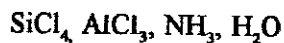


Fig 17.11: the formation of CH_4 , using sp^3 hybrid orbitals on carbon and $2s$ atomic orbitals on H atoms.

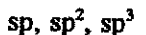
We may remember that the concept of hybridization has been devised so that the bonds in a molecule may be described in terms of localized bonding orbitals. Because of its introduction, we have been able to explain the experimentally observed shapes of molecules.

INTEXT QUESTIONS 17.2

1. What type of hybridizations is involved in each of the following :



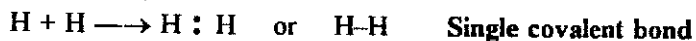
2. What shapes are associated with the following hybrid orbitals?



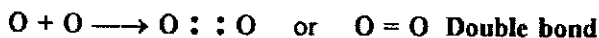
3. What hybrid orbitals are used by the central atom in BeF_2 and SF_2 ? What are resulting shapes of these molecules? Predict the bond angles.
-

17.5 MULTIPLE BONDS: SIGMA (σ) AND Pi (π) BONDS

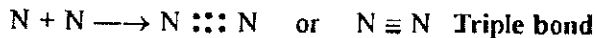
A single covalent bond is formed when the two bonding atoms share a pair of electrons. Lewis structure between two hydrogen atoms may be represented as:



The formation of oxygen molecule in terms of Lewis structure may be represented as:



Each oxygen atom shares two pairs of electrons with the other atom to complete its octet. Sometimes, three pairs of electrons may be shared between two atoms. An example of this type is the formation of N_2 .



Molecules containing double or triple bond are said to have multiple bonds.

* Boron has ground state electronic configuration, $1s^2, 2s^2 2p^1$. In order that boron may form three bonds as in BF_3 , one of the $2s^2$ electrons is promoted to a $2p$ orbital giving the excited state electronic configuration $1s^2, 2s^1, sp^2$

ORBITAL PICTURE OF MULTIPLE BONDS

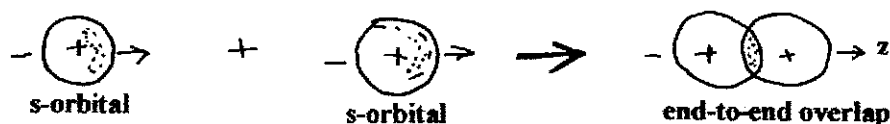
A covalent bond is formed when two atomic orbitals overlap. The extent of overlap determines their strength, i.e., the greater the overlap the stronger is the resulting bond. Depending on the type of atomic orbitals involved in bond formation, we may have different types of overlap. The resulting covalent bonds may be classified as:

(i) σ -covalent bond

(ii) π -covalent bond

A. σ - Covalent bond: Sigma (σ) bond is obtained by the end-to-end overlap of any one of these combinations of atomic orbitals. Sigma bonds are symmetrical. This type of end-to-end overlap results in the formation of a strong covalent bond.

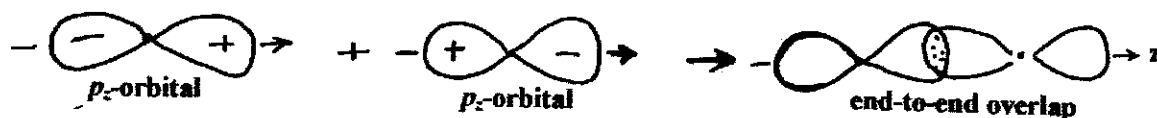
(i) s-s orbital overlap



(ii) s- p^* orbital overlap

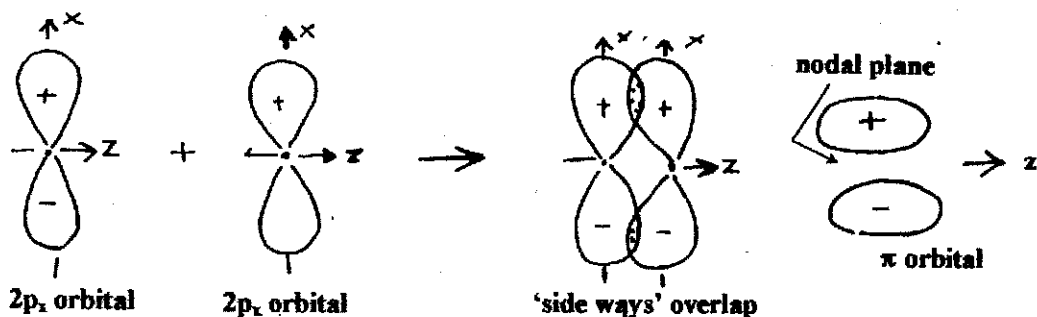


(iii) p-p (end-to-end orbital overlap)



B. π Covalent bond: The 'side - ways (or lateral) overlap between two p-orbitals, which have their lobes perpendicular to the molecular axis, results in the formation of a π -bond.

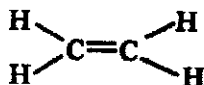
* p-orbital along x-axis is called p_x , along y-axis is called p_y and loop z-axis is called p_z .



Similarly, overlap between $2p_y$ - $2p_y$ orbitals also yields a π -bond. The side-wise overlap is not efficient and so results in a weak bond. Therefore, π -bond is a weaker bond than a σ -bond.

17.6 Bonding in Ethylene (C_2H_4) (σ - π model for the Double Bond)

Ethylene molecule has planar geometry. Each carbon atom is bonded to



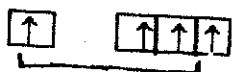
three other atoms which lie in a plane and make angles of approximately 120° with each other. The bonds may be described by using a set of three equivalent sp^2 hybrid orbitals on each of the carbon atoms. The formation of three hybridised sp^2 bonds may be explained as follows:

The ground state electronic configuration of carbon atom is $1s^2, 2s^2, 2p^2$. In the excited state one of the $2s$ electrons is promoted to the slightly higher energy vacant $2p$ orbital.

Ground state electronic configuration of carbon:



Excited state electronic configuration of carbon:



The $2s$ and two p orbitals are combined to give three sp^2 hybrid orbitals (Fig. 17.12 and 17.13).

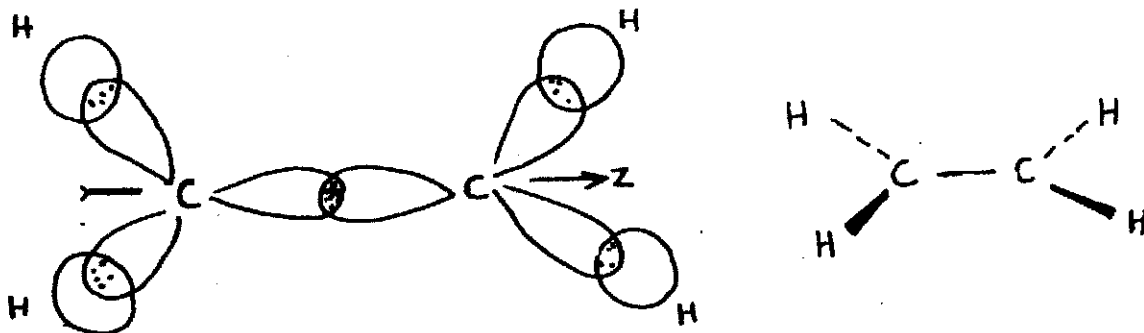
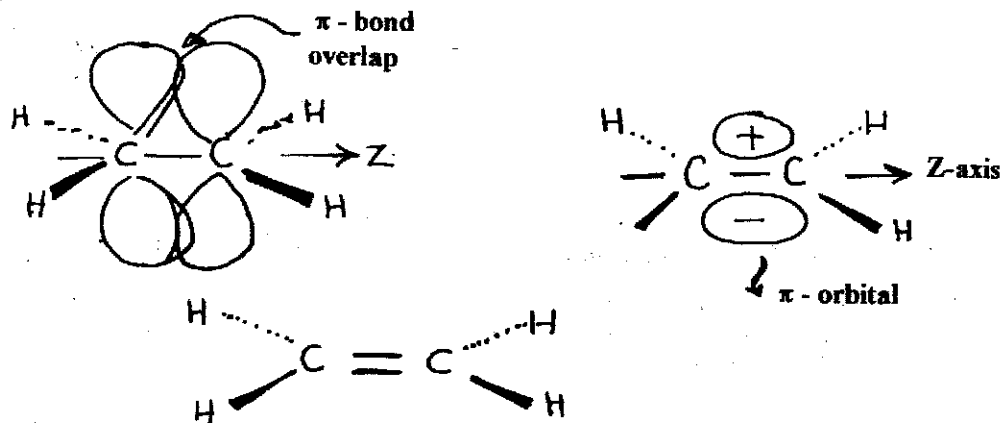


Fig. 17.12: Description of σ -bonds (only) in ethylene.

Fig. 17.13: Formation of π -bond in ethylene.

The C-H and C-C σ -bond orbitals are formed by a set of sp^2 hybrid orbitals on each carbon atom and a π -bond is obtained by 'sideways' overlap of two p-atomic orbitals. A σ -bond is symmetrical around the bond direction, but a π -bond has a planar node (low electron density) in the bond direction.

The C = C double bond thus consists of a σ -bond formed by 'end-on' overlap of sp^2 orbitals and π -bond formed by 'sideways' overlap of 2p atomic orbitals. Because of the lower strength of a p-bond, energy of

C = C double bond is less than twice the energy of C - C single bond.

A double bond thus consists of a σ -bond and a π -bond.

17.7 BONDING IN ACETYLENE (C_2H_2) (s-p MODEL FOR THE TRIPLE BONDS)

Acetylene molecule has linear geometry. Each carbon atom is bonded to



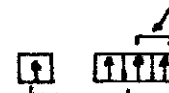
two atoms which lie on the same axis. The bonds may be described by using a set of two sp hybrid orbitals and $2p_x$ and $2p_y$ atomic orbitals.

The ground state electronic configuration of carbon atom is $1s^2, 2s^2 2p^2$. In the excited state one of the $2s$ electrons is promoted to a slightly higher energy vacant $2p$ orbital.

Ground state electronic configuration of carbon:



Excited state electronic configuration of carbon:



Form two sp hybridized orbitals

The 2s and 2p orbitals hybridize to give two sp hybrid orbitals. The sp hybrid orbitals on each of the carbon atoms are used to form localized bonding orbitals with a hydrogen 1s orbital and with an sp orbital on the other carbon atom (see Fig. 17.14). This describes the formation of C-H and C-C bonds.

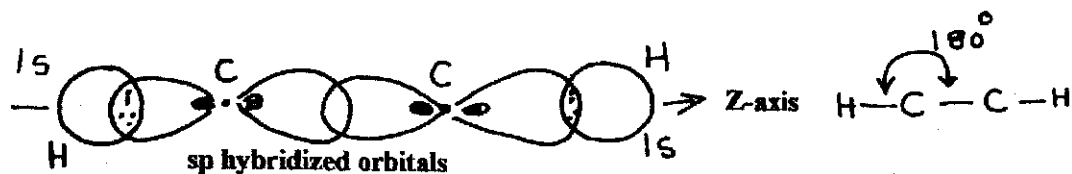


Fig 17.14: Description of σ -bonds (only) in acetylene

Two electrons, one in each orbital, remain in the 2p_x and 2p_y orbitals. These orbitals are combined with similar orbitals on the other carbon atom to form two π -bonds. These orbitals are combined in a sideways overlap (see Fig. 17.15).

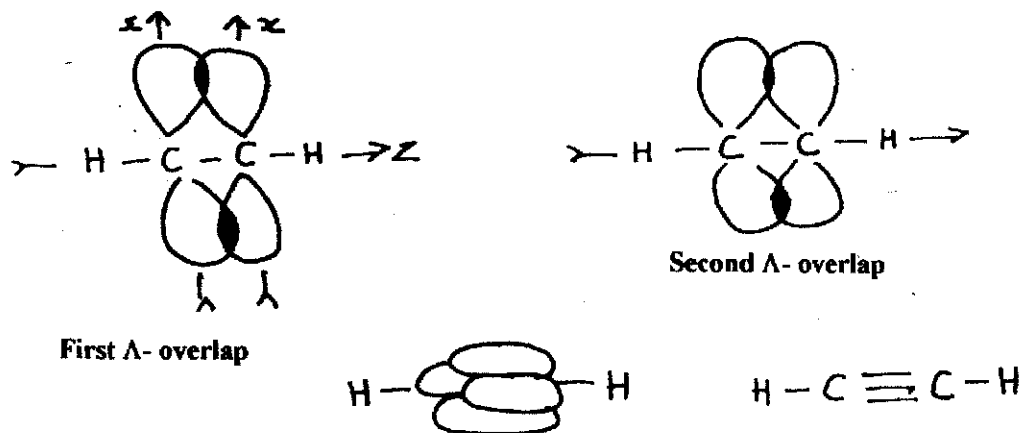


Fig 17.15: Formation of π -bonds in acetylene.

A triple bond thus consists of a σ -bond formed by an overlap of sp hybrid orbital on each carbon atom. Two π -orbitals are formed by 'sideways' overlap of the 2p_x and 2p_y atomic orbitals on each carbon atom.

INTEXT QUESTIONS 17.3

1. Explain the formation of a σ -bond and a π -bond
.....
2. What constitutes (i) a double bond and (ii) a triple bond.
.....
3. Show pictorially the formation of a σ -bond and a π -bond in O_2 molecule.
.....
4. Why is a σ -bond considered weaker than a π -bond?
.....
5. How would bond length vary amongst the following :



17.8 WHAT YOU HAVE LEARNT

- Molecules have well defined shapes (or geometries). Properties of molecules are directly related to their geometries.
 - Shapes of molecules can be easily predicted on the basis of valence shell electron pair repulsion model (VSEPR)
 - VSEPR theory states that (i) geometry of a molecule depends upon the total number of valence shell electron pairs (bonded or non-bonded) about the central atom. For example, two electron pairs around the central atom adopt linear geometry, and four pairs adopt a tetrahedral arrangement.
 - If the valence shell of the central atom contains lone pairs in addition to bond pairs then the real shape of the molecule shall be modified based on the assumption that lone pair occupies more space in the valence shell of the central atom than bond pair and the order of repulsion is,

lone pair – lone pair > lone pair – bond pair > bond pair – bond pair
 - In order to account for the linear geometry of BeF_2 or tetrahedral structure of CH_4 , atomic orbitals may be mixed to form equivalent hybrid orbitals.
 - Sigma (σ) covalent bond is obtained by the 'end-to-end' overlap of atomic orbitals. These bonds have axial symmetry.
 - Pi (π) bonds are formed due to the 'side-ways' overlap between two p-orbitals which
-

have their lobes perpendicular to the molecular axis. These orbitals have a nodal plane in the plane of the molecule.

- Ethylene (C_2H_4) molecule consists of one σ -bond and one π -bond between two carbon atoms. Each carbon atom uses sp^2 hybrid orbitals to form two C-H and one C-C σ -bonds. The third p-orbital containing a single electron on each carbon atom results in a σ -bond formation by their 'side-ways' overlap.
- Acetylene (C_2H_2) molecule contains one σ bond and two π -bonds between the two carbon atoms. Each carbon atom uses sp hybrid orbitals to form σ -bonds and the two 2p atomic orbitals containing one electron each are used in a 'side-ways' overlap to form two π -bonds.
- Carbon dioxide molecule has linear geometry. The carbon atom uses localized hybrid orbitals to form two σ -bonds with each oxygen atom. The two π -bonds are formed by the 'side-ways' overlap of $2p_x$ - $2p_x$ and $2p_y$ - $2p_y$ orbitals of carbon and oxygen.
- Nitrogen molecule contains one σ -bond and two π -bonds.

17.9 TERMINAL EXERCISES

1. What shapes are associated with the following type of hybridization? Give atleast two examples of each type: sp , sp^2 and sp^3 .
.....
2. Which combinations of p-orbitals give rise to (i) σ -bond and (ii) π - bond?
.....
3. Predict the shapes of the following molecules/ions on the basis of VSEPR model: BeH_2 , BCl_3 , NH_4^+ , $PCl_5(g)$, SF_6 .
.....
4. Explain in terms of VSEPR theory that the HOH bond angle is slightly less than the tetrahedral angle, 109.5° .
.....
5. Explain in terms of VSEPR theory that HNH bond angle is 107° while HOH is 104.5° .
.....
6. Explain the shapes of the following molecules/ions: ClF_3 , ICl_2^- , BrF_3 .
.....
7. The carbon - oxygen bond length is shorter in CO than in CO_2 molecule. Explain.
.....

8. Give the hybridization of the central atom and the geometry of the following molecules: SnCl_2 , H_2O , BF_3 , SiCl_4 .

CHECK YOUR ANSWERS

INTEXT QUESTIONS 17.1

- AX_3L , AX_4 , AX_4 , AX_4 , AX_4 , AX_3L , AX_4
- Octahedral, Square pyramid, Square planar, Linear, Tetrahedral.
- Ammonia molecule ($:\text{NH}_3$) contains three bond pairs and one lone pair. Therefore it has pyramidal shape. The fourth position of the tetrahedron is occupied by a lone pair. Since a lone pair of electrons occupy greater space around the central atom, their repulsion pushes the bond pairs slightly closer. Therefore, the tetrahedral $\angle\text{HNH}$ decreases slightly.

INTEXT QUESTIONS 17.2

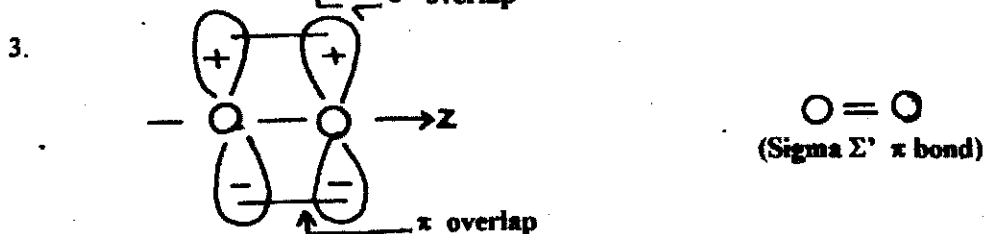
- sp^3 , sp^2 , sp^3 , sp^3
- Linear, Planar triangular, Tetrahedral.
- In BeF_2 , Be uses sp hybrid orbitals for formation of localized bonds with the F atoms. It is thus a linear molecule. In SF_2 , S atom is sp^3 hybridized. The two hybrid orbitals are used for localized bond formation with two F atoms and the other two hybrid orbitals are used by the two lone pairs on the S atom.

INTEXT QUESTIONS 17.3

- Sigma (σ) bond is formed by the end-to-end overlap of two orbitals. These orbitals have axial symmetry, i.e., they are symmetrical about the molecular axis. Combination of s-s, s-pz and pz-pz orbitals give rise to σ -bond formation (assuming Z-axis as the molecular axis).

π -bond, on the other hand, is formed by the 'side-ways' overlap of p-orbitals such as $\text{p}_x\text{-p}_x$ or $\text{p}_y\text{-p}_y$ (p-orbitals which have their lobes perpendicular to the molecular axis). The π -orbital has a nodal plane in the plane of the molecule.

- A double bond consists of one sigma bond and one pi bond and a triple bond consists of one sigma bond and two π -bonds.

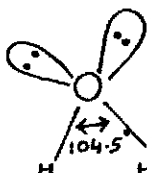


- The π -bond formation involves 'sideways' overlap of two orbitals. This type of overlap is always less effective than the end-to-end overlap leading to sigma (σ) bond formation. Thus a π -bond is always weaker than a σ -bond.
- $A \equiv A$; Triple bonded species have the shortest bond length. $A=A$; Double bonded species are longer than Triple bonded species but shorter than a single bonded molecule.

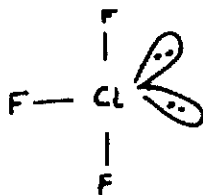
$A-A$; Single bonded species will have the longest bond length.

TERMINAL EXERCISE

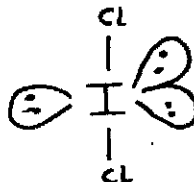
- Linear BeF_2 , $BeCl_2$, Triangular planar (BF_3 , BCl_3), tetrahedral (CH_4 , CF_4).
- σ -type bond is formed by combination of the following atomic orbitals: s-s, s-pz (z is assumed to be the molecular axis) and $2p_z-2p_z$. π -type orbital is formed by combination of p_x-p_x and p_y-p_y .
- Two bonding pairs (linear); three bonding pairs (triangular planar); four electron pairs (tetrahedral); five electron pairs (trigonal bipyramid) and six electron pairs (octahedral).
- The oxygen atom in H_2O contains a total of four electron pairs in its valence shell. Two of these are bond pairs and the other two are lone pairs localized on the central oxygen atom. Since lone pairs occupy more space than bond pairs due to greater repulsion, the HOH bond angle is decreased below the tetrahedral angle.
- Ammonia (NH_3) contains three bond pairs and one lone pair while in water (H_2O) there are two bond pairs and two lone pairs. The two lone pairs exert more repulsions than a single lone pair. Therefore.



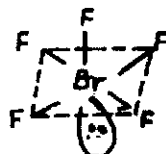
the HOH angle in water shown more contraction (than in NH_3) from the ideal tetrahedral bond angle.



- ClF_3 contains five electron pairs (7 electrons from chlorine and 3 electrons from three F atoms). Therefore, Cl has trigonal bipyramidal arrangement. Since two electron pairs are lone pairs, they occupy the equatorial sites.



ICl_2 contains 5 electron pairs [$7+2+1$ (from the -ve charge)]. Therefore it has linear geometry. BrF_5 contains 6 electron pairs ($7+5$). Since only five of these are bond pairs, therefore the geometry is square pyramidal.



7. Carbon monoxide (CO) contains one sigma and two pi bonds, i.e., it has a triple bond between carbon and oxygen (C=O). Carbon dioxide has one sigma and one π -bond between carbon and each oxygen atom (O=C=O). A triple bond is shorter than a double bond.

8. SnCl_2 : angular, sp^2 hybrid orbitals at Sn

H_2O : angular, sp^3 hybrid orbitals at O

BF_3 : planar, sp^2 hybrid orbitals at B

SiCl_4 : tetrahedral, sp^3 hybrid orbitals at Si

