THEORIES OF COVALENT BONDING AND SHAPES OF MOLECULES

Chapter 3

Teaching Periods	Assessment	Weightage
10	1	10

Students will be able to:

- **Describe** the features of sigma and pi bonds.
- **Use** VSEPR and VBT theories to describe the shapes of simple covalent molecules.
- **Describe** the shapes of simple molecules using orbital hybridization.
- **Determine** the shapes of some molecules from the number of bonded pairs and lone pairs of electrons around the central atom.
- **Define** bond energies and explain how they can be used to compare bond strengths of different chemical bonds.
- **Predict** the molecular polarity from the shapes of molecules.
- **Describe** how knowledge of molecular polarity can be used to explain some physical and chemical properties of molecules.
- **Describe** the change in bond lengths of hetero-nuclear molecules due to difference in Electronegativity values of bonded atoms.
- **Explain** what is meant by the term ionic character of a covalent bond.

INTRODUCTION

After getting detailed study about the structure of an atom in the previous chapter, the next investigation is why and how atoms combine to produce a molecule?

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"**.

Studies on chemical bond formation came to materialize during early 20th century, after the electron had been discovered. Lewis (1916) gave the concept of valency and said that electrons in atoms are responsible for chemical bonding. Electronic theory of chemical bonding which is proposed independently by Kossel and Lewis tells that a chemical bond is formed between two atoms to acquire noble gas configuration. Atoms of almost all elements have incomplete outer shell and tend to complete their outer shell by the chemical combination with other atoms. It can be done either by sharing or transfer of electrons. Atoms of noble gases are extremely stable due to the completion of duplet/octet therefore they do not form any type of chemical bond and remains exist in atomic state (mono atomic molecule). The concept of ionic bond formation is quite simple and understandable. However, the way a covalent bond forms as well as the shape of molecules can be understood on the basis of various theories.

3.1 THEORIES OF COVALENT BOND

Lewis concept for covalent bond formation provides us a guideline for writing the structural formula of various covalent compounds but neither describes the nature of bonding forces, nor about the shape of molecules and many other properties such as bond energies, bond strength and the para magnetic behavior of molecule.

There are two modern theories which describes the behavior of electron in molecule

(i) Valence Bond Theory (VBT)

(ii) Molecular Orbital Theory (MOT)

3.1.1 Valence Bond Theory

This theory was introduced by London and Heitler in 1927. This theory tells how the bonding in covalent molecule takes place by the overlapping of atomic orbitals. It not only provides basic information for analyzing the structure and the bonding in the molecule but also the strength of covalent bond as well as molecular shape on the basis of atomic orbital interaction. The main postulates of this theory are given below.

(i) A covalent bond is formed due to the overlap of half filled orbital of combining atoms. (The term overlap represents sharing of some common region in space).

(ii) As a result of overlapping there is a maximum electron cloud somewhere between the two overlapped orbital.

(iii) The electrons present in both overlapped orbital should be in opposite spin.

(iv) The strength of bond is determined by the extent of overlap. The greater the overlap, the stronger is the bond.

(v) Each atom involves in the overlapping keep its own atomic orbital but electron pair is shared up by both atoms which take part in the overlapping.

Valance bond theory describes two ways of overlapping of atomic orbital which results in the formation of following two types of covalent bonds.

(i) sigma (σ) bond

(ii) pi(π) bond

Sigma (σ) Bond:

This bond is established when the two atomic orbital overlap linearly in such a way that both orbital lie along the line joining the two nuclei. It defines as **"the bond formed by head to head overlapping of half filled atomic orbitals"**. The electron density in sigma bonded atoms found highest between the two bonded nuclei.

The formation of sigma bond results due to the following types of head to head overlapping.

s–s overlapping:

It is the overlap of half filled **s** orbital of two combining atoms. This type of overlapping exist in H_2 molecule.

Hydrogen atom contains just one electron in 1s-orbital. When the two hydrogen atoms come closer to each other, their half filled s-orbital overlap and form H–H sigma bond in which the electron cloud is rich along the axis between two nuclei.

(H atom)   (H atom)   (H₂ molecule)

1st H atom [1]

2nd H atom [↓] ← σbond
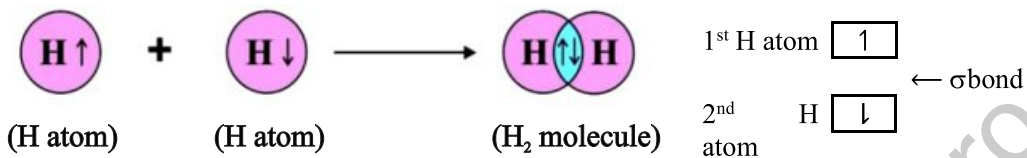
s–p overlapping:

It is the overlap of half filled **s** and half filled **p** orbital of two combining atoms. Example of molecule in which sigma bond is formed due to s-p overlapping are HF, HCl etc.

HF molecule is formed by overlap of half filled 1s orbital of hydrogen atom and half filled $2p_z$ orbital of fluorine.

(H atom)   (F atom)   (HF molecule)
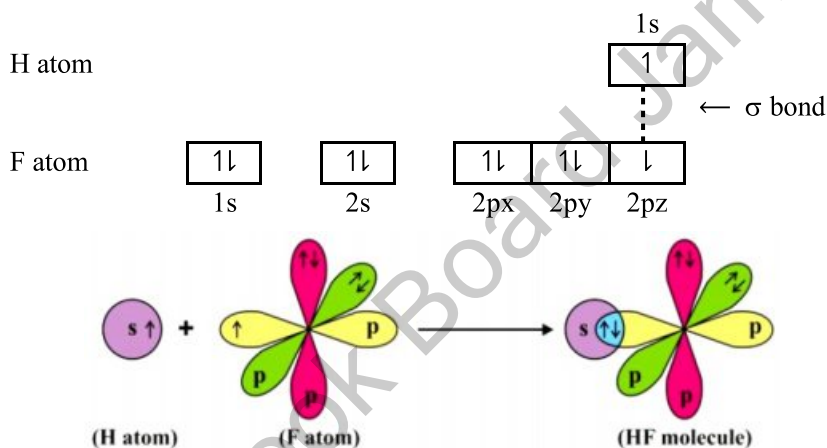
p–p overlapping:

It is the overlap of half filled **p** orbital of two combining atoms. The example of this type of overlapping is F₂ molecule.

The electronic configuration of fluorine is $1s^2\ 2s^2\ 2p_x^2\ 2p_y^2\ 2p_z^1$, it means only pz orbital is occupied by single electron and available for overlap. VBT tells that, half filled pz orbital of both fluorine atoms undergo overlapping in which the electron pair is shared up between the two atoms.


(F atom)   (F atom)   (F₂ molecule)
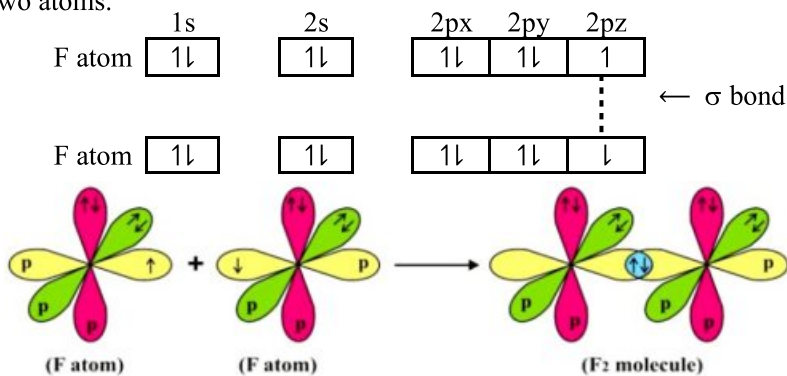
Pi(π) Bond:

This bond is formed by the lateral or side way overlap of the p-orbital between the two atoms which already bonded through sigma bond. The condition for the formation of pi bond is that the two p-orbital should be parallel to each other. The electron cloud of pi bond in unsymmetrical and is concentrated above and below the plane of sigma bond. In this situation the rotation of p-orbital become restricted between the two atoms. Since the region of overlapping of p-orbitals in the formation of pi bond is small (minimum), it is relatively weaker than sigma bond.

Example of molecules which possess pi bond are O_2 and N_2 etc.

The electronic configuration of oxygen is $1s^2$, $2s^2$, $2px^2$, $2py^1$, $2pz^1$; since there are two half filled p orbital on each oxygen atom, one of them undergoes head to head overlapping to form sigma bond while the overlapping of other p-orbital takes place laterally which lead to the formation of pi bond.

(O atom)   (O atom)   (O_2 molecule)
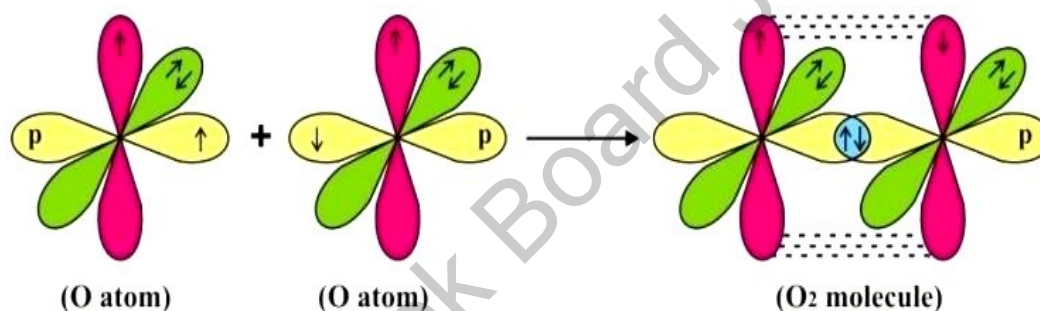
Strength of bond in term of valence bond theory

An important feature of valence bond theory is that the strength of covalent bond is proportional to extent of overlapping of atomic orbital. The greater the overlapping the stronger the bond between the atoms and the higher the energy require to break the bond.

Due to spherical charge distribution in s–orbital, generally **s–s** overlap is not so effective as **s–p** and **p–p** overlap. Since p–orbital have directional charge distribution and longer lobes which cause more effective overlap. Thus **s–s** sigma bond is relatively weak than **s–p** and **p–p** sigma bond.

In pi (π) bond the orbital has two regions of electronic density, one is above the nuclear axis and other is below the nuclear axis. This type of overlapping of atomic orbitals is not maximum that is why pi bond is weaker than sigma bond.
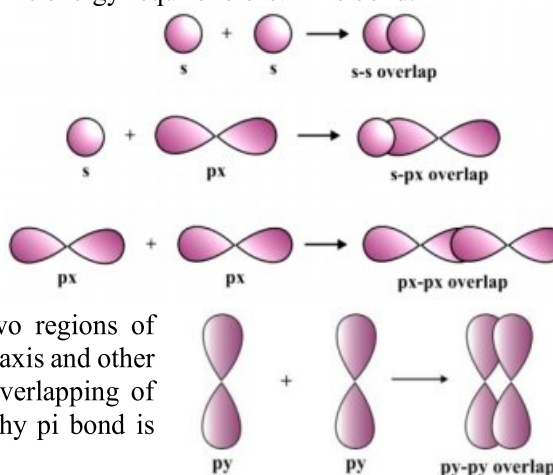
Table 3.1	Some essential features of sigma and pi bond	
Sigma Bond		**Pi Bond**
It is formed by head to head overlapping of half filled atomic orbital.		It is formed by lateral/parallel overlapping of half filled atomic orbital.
Only one sigma bond can exist between the bonded atoms.		Maximum two pi bonds can form between the two atoms.
Orbital free rotation can be possible between the two atoms if only sigma bond is present.		Orbital free rotation is not possible between the two atoms if pi bond is present.
Electron cloud is denser at the plane of bond axis.		Electron cloud is denser at above and below the plane of bond axis.

Limitation of Valance bond theory

Although VBT furnishes a good picture of bonding in molecules, however it has some short coming.

- It fails to describe the valencies in Carbon, Boron and Beryllium.
- It does not tell about para magnetic behavior of oxygen.
- It fails to describe the delocalization of electrons in the molecule.

Self Assessment

(i) Why sigma bond is stronger than pi bond?

(ii) Why p-p sigma bond is stronger than s-s and s-p?

3.1.2 Molecular Orbital Theory

Mullikan, Hund and Huckel (1927) developed an alternate theory known as molecular orbital theory to overcome the short comings of VBT. Assumptions of molecular orbital theory are given as:

(i)   Atomic orbitals of similar energies linearly combine together to produce molecular orbitals.

(ii)   Combination of two atomic orbitals (A.O) gives two molecular orbitals (MO) one of them has lower energy and other has higher energy than any of the atomic orbital from which they formed.

(iii)   The molecular orbital with lower energy is called as bonding molecular orbital (BMO) and the orbital with higher energy is called as anti bonding molecular orbital (ABMO).

(iv)   The movement of electrons in M.O is influenced by both nuclei of combining atoms.

(v)   The filling of electrons into the molecular orbital is followed by fundamental rules of electronic configuration i.e. Aufbau principle, Hund's rule and Pauli rule.

Characteristic of Bonding and Anti Bonding M.O

Bonding molecular orbital has lower energy than atomic orbital from which it is formed. Electrons in the bonding molecular orbitals favour bonding because combining orbital interact constructively thus the probability of electron density is maximum between the two nuclei.

Anti bonding molecular orbital has higher energy than the two combining atomic orbital. It is produced due to destructive interaction and hence electron density in the region between two nuclei is zero since the nodal plane bisecting the inter nucleus axis.

Molecular orbital theory (MOT) is best to predict the bond order and the magnetic properties of molecules. The formula used in determining the bond order is given as.

$$\text{Bond order} = \frac{N(b) - N(a)}{2}$$

Where

N(b) = Electrons in bonding M.O
N(a) = Electrons in anti bonding M.O

Molecular orbital diagram for some homonuclear diatomic molecules are describe below.

Fig 3.1: Description of the formation of molecular orbital in
(a) H_2 molecule (b) HF molecule (c) F_2 molecule

H_2 – molecule

Hydrogen atom contains one electron in 1s orbital. The atomic orbital of both hydrogen atom linearly combine to form two molecular orbitals. According to the rule of electronic configuration, electrons accommodate in bonding MO since it possess low energy hence anti bonding MO remains vacant. This can be illustrated in the molecular orbital diagram.

Bond order of H_2 molecule is determine as

$$\text{Bond order of } H_2 = \frac{N(b) - N(a)}{2} = \frac{2 - 0}{2} = 1$$

Since there is no unpaired electron in any molecular orbital, hydrogen is diamagnetic in nature.

**Fig 3.2: Molecular orbital energy diagram of H_2 molecule**
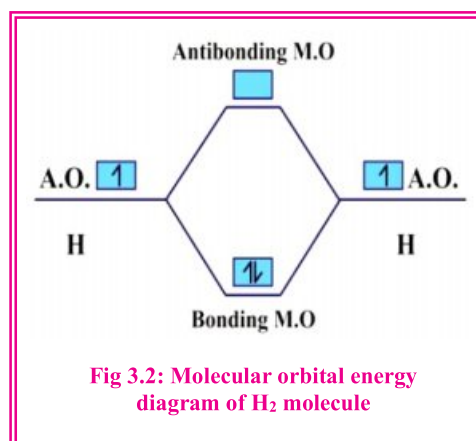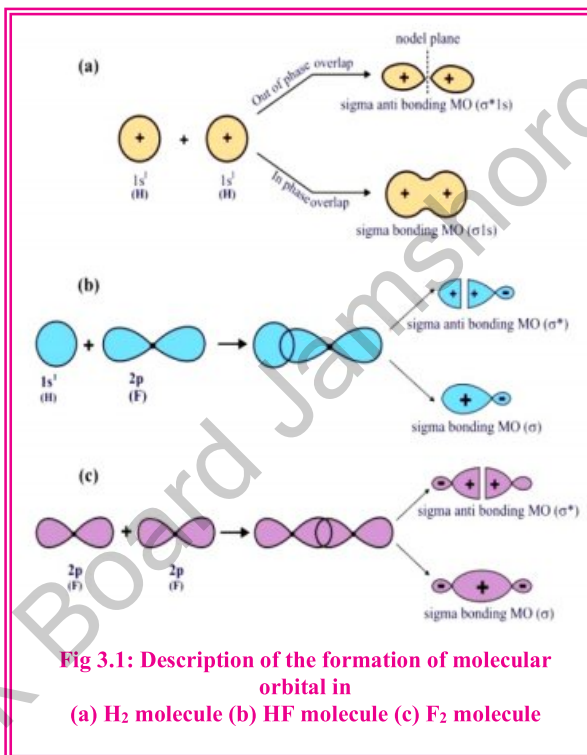
O₂ – molecule

The electronic configuration of oxygen $(z = 8)$ is $1s^2, 2s^2, 2p^4$. Thus there are five atomic orbitals with eight electrons in each oxygen atom. These five atomic orbitals of both oxygen atoms combine to form ten molecular orbitals as shows in molecular orbital energy diagram.

Bond order of O_2 molecule is determine as

$$\text{Bond order of } O_2 = \frac{N(b) - N(a)}{2} = \frac{10 - 6}{2} = 2$$

Since there are two unpaired electrons in anti bonding MO, O_2 is paramagnetic.

The molecular orbital configuration with increasing energy order is given as
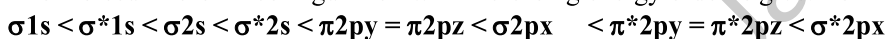
$\sigma 1s < \sigma^*1s < \sigma 2s < \sigma^*2s < \pi 2py = \pi 2pz < \sigma 2px < \pi^*2py = \pi^*2pz < \sigma^*2px$
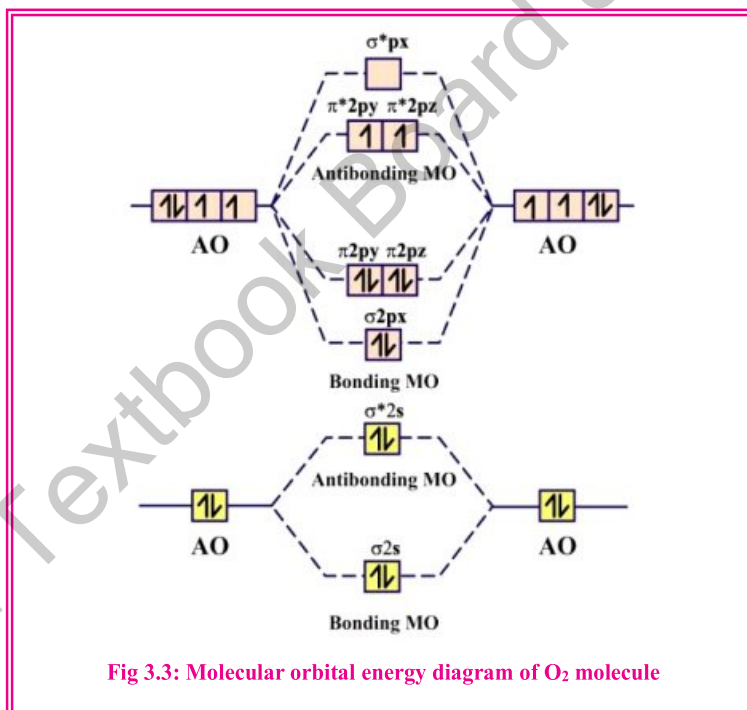
Fig 3.3: Molecular orbital energy diagram of O₂ molecule

Self Assessment

Write the molecular orbital energy diagram of N₂ molecule and determine its bond order. Also predict whether it is paramagnetic or diamagnetic?

Valence Bond Theory	Molecule Orbital Theory
Valence Bond theory tells that only some valence electrons are involved in the bond formation.	Molecular orbital theory tells that bond formation occurs due to the involvement of all the valence electrons of interacting atoms.
According to valence bond theory, both the concerned atomic orbitals possess their individual identity.	According to the molecular orbital theory, both the concerned atomic orbitals donot possess their individual identity.
VBT doesn't introduce any adequate idea about the bond order.	MOT gives adequate idea about the bond order by virtue of which, the bond can be identified as single, double or triple bond.
The paramagnetic behavior of molecules such as oxygen molecule (O_2) cannot be explained by valence bond theory.	The paramagnetic behavior of molecules are very well explained using molecular orbital theory.

3.2 SHAPE OF THE MOLECULES

Simple poly atomic molecules and ions generally acquire linear, tetrahedral, pyramidal and angular shapes etc. These shapes can be determined experimentally, however also predicted on theoretical basis. Beside VBT there are two more significant theories which describe the shape of molecule.

(i)   Valence shell electron pair repulsion theory (VSEPR)
(ii)   Hybridization

3.2.1 Valence Shell Electron Pair Repulsion Theory (VSEPR)

This approach to the structure of a covalent molecule is due to sidgwick and powell (1940). They pointed out that the shapes of molecules can be determined by the repulsion between the electron pairs present in valence shell of central atom.

The main postulates of this 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 of central atom which do not take 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.

Do You Know?

Multiple bond (double and triple) is treated as single bond in VSEPR because π bonds do not alter the basic idealized geometry of a molecule.

4. The force of repulsion between lone pairs and bond pairs is not the same. The order of repulsion is as follow.
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).

Prediction of Five Basic Shapes by VSEPR
Linear Shape
This shape is found in AX_2 type molecules in which the central atom (A) contains two bond pairs only. The equal repulsion of these two bond pairs of electrons extend the corner atoms (X) at 180° angle and makes linear shape.
Example of molecules having linear geometry are $BeCl_2$, C_2H_2, CO_2 etc.
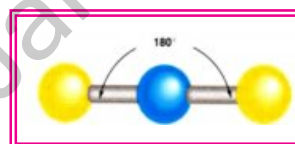
Trigonal Planer Shape
This shape is found in AX_3 type molecules where the central atom (A) possesses only three bond pairs of electrons. The equal repulsion of these bond pair electrons orient the three corner atoms (X) at 120° and the geometry thus developed is trigonal planar.
Examples of some molecules which acquire trigonal planar geometry are BF_3, C_2H_4, $AlCl_3$ etc.
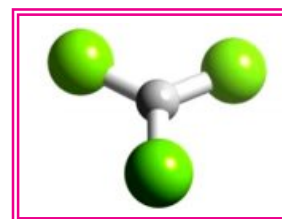
Tetrahedral Shape
Molecules which have tetrahedral shape are categorized into AX_4 type. Here the central atom (A) contains four paired electrons. The repulsion of these four electron pairs directed the four X atoms towards the corner of a tetrahedron. The angle settled in this type of repulsion is 109.5°.
Examples are CH_4, C_2H_6 etc.
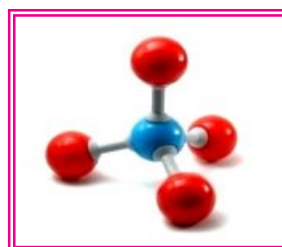
Trigonal Pyramidal Shape
This is a cone like shape with a tetrahedral base and found in the molecules of AX_3E type where A is the central atom, X are the corner atoms and E is lone pair of electron in central atom.
The central atom in this type of molecules is surrounded by three bond pairs and one lone pair of electron of its own. Since the repulsion of lone pair of electrons is more effective than bond pair electrons, a
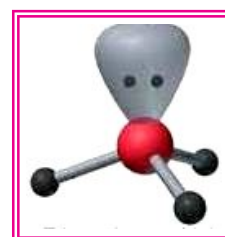
slight distortion in the tetrahedral shape occur by narrowing the angle at one side from 109.5° to 107°. It makes a pyramidal shape.

Examples are NH_3, PH_3 etc.

Angular Shape

Common examples of molecules having angular shape are H_2O, H_2S etc. This is an AX_2E_2 type shape in which A is central atom, X are two corner atoms and E_2 are two lone pair of electrons present in central atom.
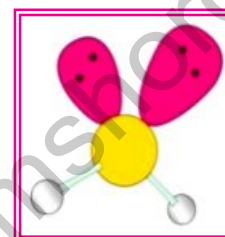
There are two bond pair and two lone pair electrons around the central atom which initially makes a tetrahedral geometry in which two ends of tetrahedron are filled with two lone pairs and the other two corners occupied by bond pairs. Since the lone pair repulsion is greater than bond pair repulsion, the two bond pairs deviate from the lone pair and come near to each other at 104.5°. This makes a distortion in the tetrahedral geometry and develops an angular shape.

|	**Table 3.2**			**Shape of molecule according to VSEPR theory**		
Type	**Active Electron pair**	**Bond Pairs**	**Lone Pairs**	**Molecular Geometry**	**Shape**	**Examples**
AX_2	2	2	0	Linear		$BeCl_2$ CO_2
AX_3	3	3	0	Trigonal Planar		BF_3 $AlCl_3$ BH_3
AX_4	4	4	0	Tetrahedral		CH_4 $SiCl_4$ CCl_4
AX_3E	4	3	1	Trigonal Pyramidal		NH_3 NF_3 PH_3
AX_2E_2	4	2	2	Angular or Bent		H_2O H_2S

Example 3.1

Predict the shape of CH₄, NH₃, H₂O and CO₂ molecules on the basis of VSEPR.
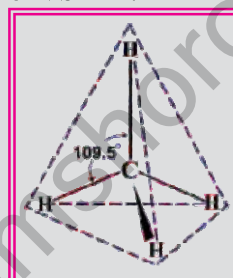
CH₄ – molecule

We begin by drawing a Lewis structure to determine the number of electron pairs around the central atom.
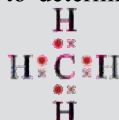
No. of Bond pair electrons = 4
No. of Lone pair electrons = 0

According to VSEPR, these four electron pairs repel to each other and directed towards the corner of tetrahedron at an angle of 109.5° hence the geometry of molecule is **tetrahedral.**

NH₃ – Molecules

Lewis structure of NH₃ molecule is drawn as
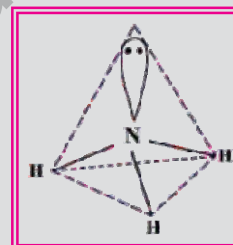
This shows the following information
About central atom
Bond pair of electrons = 3
Lone pair of electrons = 1

According to VSEPR, the repulsion of lone pair is stronger which reduce the bond angle from 109.5° to 107°.

Hence the predicted shape of NH₃ molecule is trigonal pyramidal

H₂O – Molecule

Lewis structure of H₂O molecule is drawn as

Electronic information around the centre atom is given as
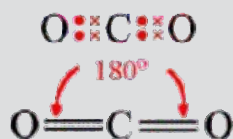No. of Bond pair electrons = 2
No. of Lone pair electrons = 2

The repulsion of two lone pair electrons reduces the bond angle from 109.5° to 104.5°.

Hence the shape of H₂O molecule is Angular

CO₂ – Molecule

The Lewis structure of CO₂ molecule is drawn as

This shows that two sigma and two pi bond exists in the molecule. According to VSEPR theory pi bond are not involved in the repulsion and geometry because these are inactive electron pairs. Since only two active electron pairs are found around the carbon atom, its shape is Linear.
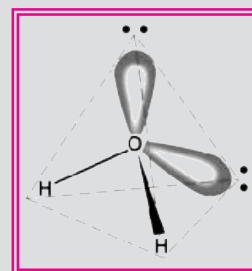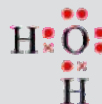
Do You Know?

In many molecules, there are more than one central atoms. In these molecules we analyze one central atom at a time to determine the active sets of electron and to predict the geometry of molecule.
For example: in ethene molecule we first considered the left hand carbon atom to analyze the geometry of molecule then we carry out a similar analysis for right hand carbon atom.

Self Assessment

According to VSEPR model, what molecular shape would you predict for
(i) BF_3 (ii) CS_2 (iii) CBr_4

3.2.2 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.

      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 tetravalent respectively.

      To account for the valency of such elements, it is assumed that some of the paired electrons are uncoupled and promoted to the orbital 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.

| Table 3.3	Ground state and excited state configuration of Beryllium, Boron & Carbon		
Elements	**Atomic No.**	**Ground state**	**Excited state**
Be	4	$1s^{1\downarrow}\ 2s^{1\downarrow}\ 2px\ 2py\ 2pz$	$1s^{1\downarrow}\ 2s^{1}\ 2px^{1}2py\ 2pz$
B	5	$1s^{1\downarrow}\ 2s^{1\downarrow}\ 2px^{1}2py\ 2pz$	$1s^{1\downarrow}\ 2s^{1}\ 2px^{1}\ 2py^{1}\ 2pz$
C	6	$1s^{1\downarrow}\ 2s^{1\downarrow}\ 2px^{1}\ 2py^{1}\ 2pz$	$1s^{1\downarrow}\ 2s^{1}\ 2px^{1}\ 2py^{1}\ 2pz^{1}$

      Linus pauling settled this disparity by suggesting the idea that the atomic orbital having nearly equal energies can be mixed in various ways within an atom to form equivalent hybrid orbital. **"The mixing of different atomic orbital to produce the same number of equivalent orbital, having same shape and energy is known as hybridization"**. The orbitals so formed are called hybrid orbital and are designated according to the number of mixing orbitals.

Table 3.4	Types of hybridization due to mixing of s and p orbitals			
Mixing Orbital	**No. and type of Hybrid orbital produced**	**Type of Hybridization**	**S Character %**	**P Character %**
One **s** and three **p**	Four sp³ orbitals	sp^3	25	75
One **s** and two **p**	Three sp² orbitals	sp^2	33.33	66.66
One **s** and one **p**	Two sp orbitals	sp	50	50

sp³ Hybridization:

"**Combination of one s and three p orbitals to produce four sp³ hybrid orbitals is known as sp³ or tetrahedral hybridization**". The hybrid orbitals are different than the pure **s** or **p** orbitals; they possess the character of both **s** and **p** orbital in the ratio of 1:3. These sp³ orbitals are directed towards the four corners of regular tetrahedron in which each angle is 109.5°.


Fig 3.4: Mixing of 2s, 2px, 2py and 2pz orbital to produce four sp³ hybrid orbitals
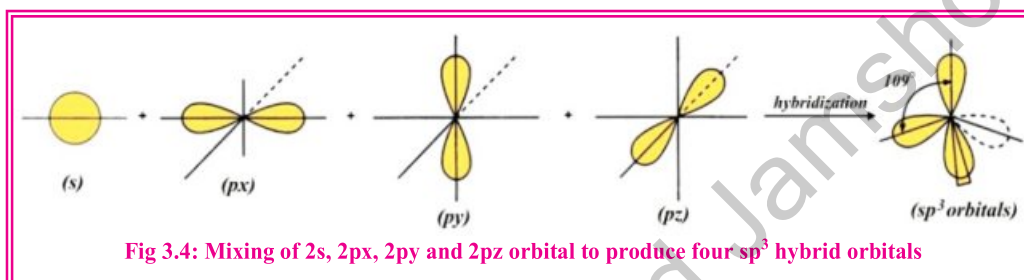
Methane Molecule (CH₄)

The electronic configuration of carbon is ($1s^2$, $2s^2$, $2px^1$, $2py^1$, $2px^0$) but it is assumed that one electron of 2s orbital get promoted to 2pz orbital to make it tetravalent.

C (z = 6) $1s^2$, $2s^1$, $2px^1$, $2py^1$, $2pz^1$ (tetravalent)

In methane, the four atomic orbital of carbon undergo a mixing process to produce four new orbital of equal energy and shape, each named as sp³ hybrid orbital.

All four sp³ hybrid orbital then directed towards the corner of a regular tetrahedron at an angle of 109.5°. Since each sp³ hybrid orbital has one electron, it overlaps with 1s orbital of hydrogen atom. Thus four C–H sigma bonds are formed.
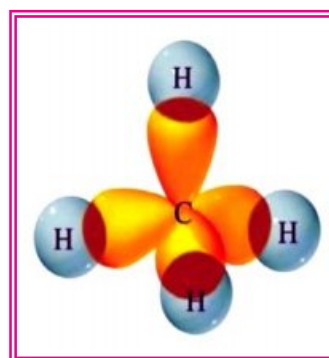
Ammonia Molecule (NH₃)

The electronic configuration of Nitrogen is $1s^2$, $2s^2$, $2px^1$, $2py^1$, $2pz^1$. Thus according to the concept of hybridization one **s** and three **p** orbital of the valence shell of nitrogen undergo the process of mixing to give four **sp³** hybrid orbital which are directed towards the four corners of tetrahedron.

Out of four hybrids orbital three have single electrons hence they overlap with s-orbital of hydrogen and form three (N-H) sigma bonds. The fourth **sp³** orbital which has lone pair of electron remains unbonded. The stronger repulsion of this orbital deviate the bond angle from 109.5° to 107° and give rise to a pyramidal geometry.
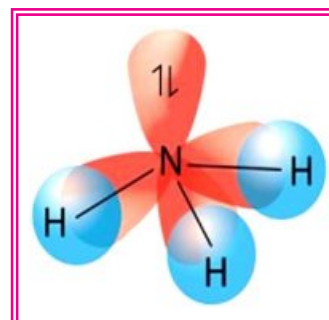
Water Molecule (H₂O)

The electronic configuration of oxygen is $1s^2$, $2s^2$, $2px^2$, $2py^1$, $2pz^1$. The four outer shells orbitals are assumed to be mixed together which results in the formation of four new sp^3 hybrid orbitals which are directed at the corner of tetrahedron.


Since only two sp^3 orbitals possess single electrons, they overlap with s-orbital of hydrogen to form two O–H sigma bonds. The remaining two sp^3 hybrid orbital contain lone pair of electrons.

Because the repulsion of lone pair is greater than bond pair, the shape of water molecule is not regular tetrahedron. The distortion of bond angle from 109.5° to 104° makes an angular geometry.
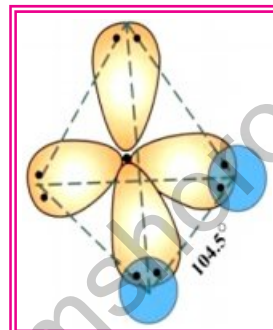
sp² – Hybridization:

"The mixing of one s and two p orbital to produce three sp² hybrid orbital is referred to as sp² (trigonal hybridization)". These orbitals are co-planar and directed towards the corners of an equilateral triangle (trigonal) at angle of 120° to each other. **sp²** orbital are different than either **s** or **p** orbital and they are considered to have a character that is one third **s** and two thirds **p**. The fourth **p** atomic orbitals which is not involved in hybridization remains unhybridized at right angle to the plane of the **sp²** orbitals.

Fig 3.5: Mixing of s, px and py orbitals to produce three sp² hybrid orbitals
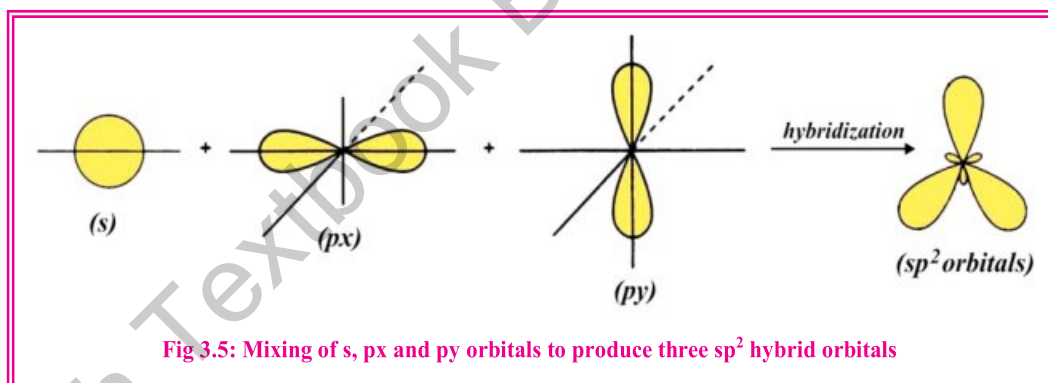
sp² hybridization provides a good model for describing the geometry of the molecules which contain carbon bonded to only three other atoms or groups, such as ethylene (C_2H_4) or Boron trifluoride (BF_3).

### Boron Trifluoride Molecule (BF₃)

The electronic configuration of Boron in ground and excited state is given as

1s	2s	2px	2py	2pz	
↑↓	↑↓	↑			(Ground state)
↑↓	↑	↑	↑		(Excited state)

One half filled **s** orbital and two half filled **p** orbital undergo the process of hybridization to produce three **sp²** hybrid orbitals. These three **sp²** hybrid orbitals lie in the same plane (coplanar) with an angle of 120° and make a planer triangular geometry.

These three **sp²** orbitals of Boron then overlap with three **p** orbital of different fluorine atoms.
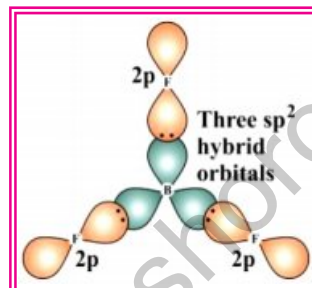
Ethene molecule (C₂H₄)

Ethene molecule consists of two central carbon atoms. Each carbon possesses three sp² hybrids orbital and one unhybrid pz orbital.

These three **sp²** hybrid orbital arrange themselves in triangular planar geometry at 120° angle. Two **sp²** orbitals of each carbon then overlap with s orbitals of two hydrogen atoms to form two C-H sigma bonds. The third **sp²** orbital of both carbon atoms overlap linearly with each other to form a C-C sigma bond. The unhybrid pz orbital of both carbon atoms which lie at right angle overlap side wise to form a pi bond.
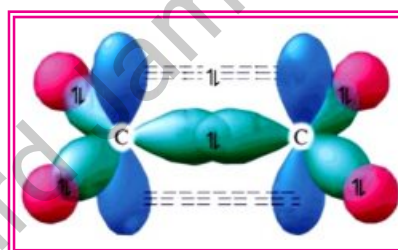
sp Hybridization:

The hybridization of one **s** and one **p** atomic orbital leads to two hybrid orbitals known as **sp** hybrid orbital. These orbitals are co-linear at an angle of 180° which provides maximum separation and overlap. Each sp hybrid orbital has 50% s character and 50% **p** character (1:1 ratio). The other two **p** orbitals remain unhybridized and are oriented at the right angles to each other and to the plane of hybrid orbitals.

Do You Know?

s-character in sp³, sp² and sp hybridization is 25%, 33% and 50% respectively. The greater the s-character the more close the electron to the nucleus and the stronger the bond. Thus sp hybridized orbital form relatively stronger bond.

Fig 3.6: Mixing of one s and one px orbitals to produce two sp hybrid orbitals
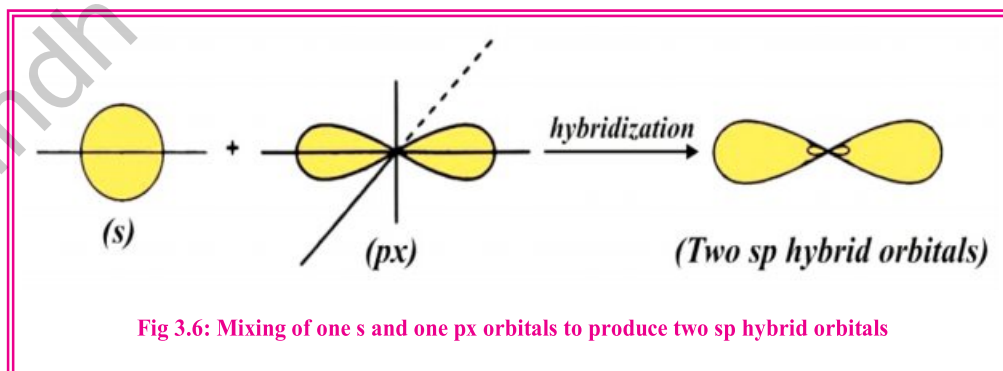
Ethyne Molecule (C_2H_2)

The type of hybridization in each carbon atom of ethyne is **sp** where as only **s** and **px** orbitals involve in the mixing process while the **py** and **pz** orbitals remain unhybridized. The two **sp** orbitals are inclined to each other at 180° angles where as the two unhybrid orbitals (**py** and **pz**) lie at right angle to the hybrid orbital as well as to each other.
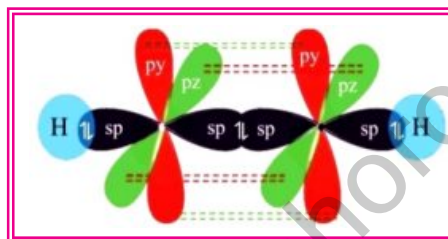

The two hybrid orbitals (**sp**, **sp**) and the two atomic orbitals (**py** and **pz**) contain single electron.

Each carbon utilizes its one **sp** orbital to overlap with **s** orbital of hydrogen while other **sp** orbital is involved in sigma bonding between the two carbon atoms. Thus overall three sigma bonds are formed at 180° angles which makes linear geometry. The unused **p** orbital lying parallel to each other undergoes side wise overlapping to form two pi bonds. One sigma and two pi bonds between the carbons atoms of ethyne molecule is identified as triple bond.

Beryllium Chloride ($BeCl_2$)

The excited state electronic configuration of Beryllium is $1s^2$, $2s^1$, $2px^1$, $2py$, $2pz$ indicates that 2s and 2px orbitals of Beryllium should involve in the mixing process and hence the result is the production of two **sp** hybrid

orbitals. Two **sp** hybrid orbitals of Beryllium overlap with p orbitals of two chlorine atoms in straight line at 180° angle. The linear geometry of molecule is due to the maximum repulsion of two electron pairs.
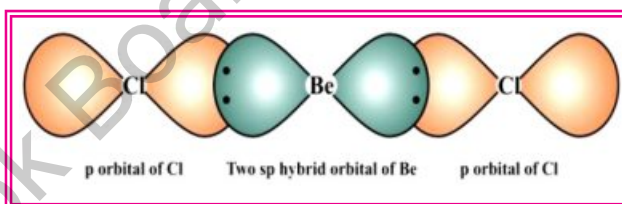
3.3 BOND CHARACTERISTICS

There are various characteristics of a chemical bond such as bond length, bond energy, bond order, dipole moment etc. All of these describe the strength and stability of bond.

3.3.1 Bond Energy

The formation and decomposition of chemical bond are two opposite processes, both associated with energy change. Bond formation is exothermic process and bond breaking is endothermic process. **"The energy involved for the breaking / formation of 1 mole of particular type of bonds in the molecule is known as bond energy"**. Alternatively the bond energy might be taken as energy released in the formation of a bond from its free atoms. It is important to note that the measurement of energy in bond dissociation is more accurate than the bond formation, thus the bond energy is generally considered as bond dissociation energy and written in term of positive sign. Since chemical reactions take place at constant pressure, the term enthalpy is often used. It is the energy required in KJ for the breaking of one mole bonds in the given sample of reactant.

$$O_{2(g)} \longrightarrow O_{(g)} + O_{(g)} \ (\Delta H = +495 \ KJ/mol)$$
$$O_{(g)} + O_{(g)} \longrightarrow O_{2(g)} \ (\Delta H = -495 \ KJ/mol)$$
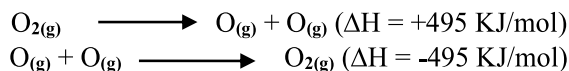
Comparison of bond energy with bond strength

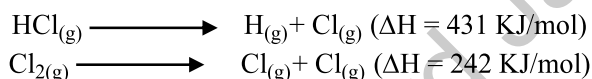Bond energy is very useful tool in determining the strength of a bond and hence help in understanding chemical reactivity. Bond energy and the strength of bond can be predicted on the basis of molecular polarity, radii of bonded atoms and the bond order.
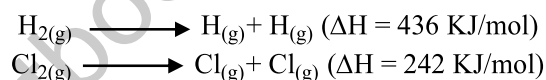
(i) Polarity of molecule

The value of bond energy in diatomic molecule depends upon whether the molecule is homo diatomic or hetero diatomic. The bond energy of hetero diatomic molecule is relatively higher since atom lie closer due to the presence of ionic character on the bonded atom.

$$HCl_{(g)} \longrightarrow H_{(g)} + Cl_{(g)} \ (\Delta H = 431 \ KJ/mol)$$
$$Cl_{2(g)} \longrightarrow Cl_{(g)} + Cl_{(g)} \ (\Delta H = 242 \ KJ/mol)$$

In the above atomization processes, we noted that the bond energy of HCl is higher due to polarity in the molecules.

(ii) Size of the bonded atoms

The value of bond energy can be correlated with the size of atoms. Two atoms of smaller size are bonded more strongly due to short inter nuclear distance thus they can be broken if high energy is provided. For example,

$$H_{2(g)} \longrightarrow H_{(g)} + H_{(g)} \ (\Delta H = 436 \ KJ/mol)$$
$$Cl_{2(g)} \longrightarrow Cl_{(g)} + Cl_{(g)} \ (\Delta H = 242 \ KJ/mol)$$

The high bond energy is due to smaller size of hydrogen atoms. Thus not only the polarity but also the size of atoms in the molecule involve in bond energy.

(iii) Presence of multiple bonds

Generally molecules with multiple bonds require high bond energy for the dissociation. Consider the bond energies involve in carbon – carbon bond breaking.

C – C (348 KJ/mol)
C = C (614 KJ/mol)
C ≡ C (839 KJ/mol)

This shows that the greater the number of bonds between two atoms, the higher the bond energy. It may be noted that the bond energy of C = C is not exactly double to that of C – C and similarly the bond energy of C ≡ C is not exactly three times higher. The reason is that double bond between the two atoms express one sigma and one pi bond. Since the pi bond is relatively weak and requires less energy for the breaking, the same reason is for C ≡ C.

Table 3.5	Average bond energies of some single and multiple bonds (KJ/mol)		
Single Bond	Bond Energy (KJ/mol)	Multiple Bond	Bond Energy (KJ/mol)
H – H	436	C = C	614
Cl – Cl	242	C = N	615
C – C	348	C = O	799
C – H	413	O = O	495
H – Cl	431	S = O	523
H – F	567	C ≡ C	839
H – O	463	N ≡ N	941
H – N	391	C ≡ N	891

Self Assessment

(i) What are the various parameters which correlate bond energy with bond strength?
(ii) Why is the bond energy of multiple bond greater than single bond?

3.3.2 Bond Length

Molecule is the combination of atoms and formed by mutual sharing of electrons. Atoms in a molecule are located at a certain distance to balance the attractive and repulsive forces between nucleus and electrons. **"The distance between the nuclei of two bonded atoms in a molecule is known as bond length"**. Since the bonded atoms are always in vibrational motion due to their kinetic energy, precise bond length cannot be determined and hence we take the average of the bond length. Bond length is experimentally determined by x-ray diffraction technique. Bond length is a very small distance and the unit use for its measurement is Angstrom (Å) which is equal to 10^{-10}m.

Bond length is a characteristic of bond which describes the strength of bond. The shorter the bond length the stronger is the bond. We can mainly correlate the bond length with the following two parameters.

(i) Bond order: The greater the number of bonds between the two atoms, the shorter the bond length. For instance, the bond length in C ≡ C is shortest than C = C and C–C.

Do You Know?

A covalent radius is the half of bond length between the nuclei of two identical atoms which are bonded through single covalent bond.

(ii) Bond polarity: The bond length between two different atoms is generally higher than similar atoms and its value depends upon the extent of polarity. For example bond length of H – Cl (1.27Å) is shorter than Cl – Cl (1.99Å).

| Table 3.6	Bond length and bond energies of some bonds	
Covalent Bond	Bond Length	Bond Energy
C – C	1.54 Å	348 KJ mol^{-1}
C = C	1.34 Å	614 KJ mol^{-1}
C ≡ C	1.20 Å	839 KJ mol^{-1}
Cl – Cl	1.99 Å	242 KJ mol^{-1}
O = O	1.21 Å	495 KJ mol^{-1}
N ≡ N	1.10 Å	941 KJ mol^{-1}

3.3.3 Ionic Character of Covalent Bond

When two different atoms having different electronegativities unite through covalent bond, a partially positive charge produced on less electronegative atom and a partially negative charge on high electronegative atom. The molecule now said to be polar bearing ionic character on its two oppositively charge poles and the bond exist between the two atoms is known as polar covalent bond.

Let consider the example of hydrogen chloride. The electronegativity of hydrogen (2.1) is less than chlorine (3.0), therefore shared electron pair is more shifted towards chlorine atom which results in appearing an ionic character on the covalent molecule.

$$H \overset{\cdot}{\underset{\times}{}} Cl \longrightarrow \overset{+\delta}{H} - \overset{-\delta}{Cl}$$

Since ionic character of covalent bond is mainly depends upon electronegativity difference between the two joined atoms, the strength of polar bond can be attributed by taking E.N difference as a primary tool. However size of the atom and bond length is also influencing factors for the bond strength. The electronegativities of some common elements in their relative order are given as.

H < I < C & S < Br < N & Cl < O < F
(2.1) (2.4) (2.5) (2.8) (3.0) (3.5) (4.0)
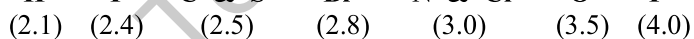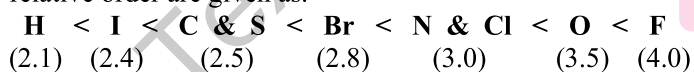
When the difference of E.N of the two atoms is almost same then relative size of atoms decide the strength of ionic character.

Do You Know?

Bond energy, bond length and bond order are three essential bond parameters which describe the strength of covalent bond.

Table 3.7	Percent polarity in some common bonds	
Bond	EN Difference	Ionic Character
Cl – Cl	0	0
H – F	1.9	43%
H – Cl	0.9	17%
H – Br	0.7	12%
H – I	0.3	6%
C – H	0.4	4%
O – H	1.4	39%
C – Cl	0.5	10%

3.3.4 Dipole Moment

We have learnt in previous section that when a molecule is assembled by two atoms of different electronegativities, a partially positive and negative charge create on the two ends. The net magnitude of this positive and negative charge in a diatomic molecule is equal and thus the molecule is electrically neutral and said to be dipole. Dipole moment is a measuring scale use for the degree of polarity of polar bond. It defines as **"The product of magnitude of charge and the distance between positive and negative centers"**. The net molecular moment is indicated by ($\rightarrow$) since dipole moment is a vector quantity.

Dipole moment = q . d

It is noted experimentally that the charge (q) is of the order of 10^{-10} esu and the distance between positive and negative centre (d) is in the range of 10^{-8} cm. Therefore dipole moment of all polar molecules found in the limit of 10^{-18} esu.cm. This quantity is known as Debye (D) after the name of introducer (Peter Debye).

1 Debye = 1×10^{-18} esu.cm
The S.I unit of Dipole moment is Coulomb meter (Cm). The inter relation between Debye and columb meter is written as
1 D = 3.336×10^{-30} Cm

Molecular polarity and the shape of molecules

Dipole moment of a molecule depends not only upon the polarity of its bonds but it also depends upon the geometry of molecule. For example H_2O and CO_2 both contain polar bonds but the angular structure of H_2O results in a dipole moment of 1.85D and said to be polar molecule. CO_2 on the other hand has zero dipole moment. Although both (C = O) bond in CO_2 are polar but directed equally on the opposite side at 180° angle making a linear geometry thus the molecule is non polar.
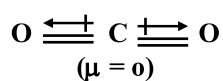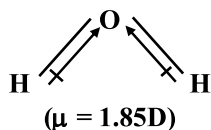

$(\mu = 1.85D)$ $(\mu = 0)$

| Table 3.8 | Dipole moment of some common substances in Debye | | |

Compound	Dipole moment (D)	Compound	Dipole moment (D)
H_2O	1.85	CH_3Cl	1.45
NH_3	1.49	C_2H_5OH	1.69
HCl	1.03	CO_2	0.00
HBr	0.78	CS_2	0.00
HI	0.38	CH_4	0.00
H_2S	0.95	H_2	0.00

Self Assessment

Which of the following molecules have dipole moment? In each case give a reason for your answer.

$CHCl_3$, SCl_2, H_2O, CO_2

3.4 EFFECT OF BONDING ON PHYSICAL AND CHEMICAL PROPERTIES

The nature and strength of bond affect on various physical and chemical properties of a substance such as solubility, melting point, boiling point, rate of reaction etc.

3.4.1 Solubility of Polar and Non Polar Covalent Compounds

It is well established that certain substances dissolve in liquid solvent while others are not. The criteria for deciding of solubility is to know whether they are polar or non polar. Many organic compounds are non polar in nature and cannot be dissolved in water however soluble in organic solvents. The solubility of covalent compound depends upon chemical nature of solvent and the substance to be dissolved.

(i)   Solubility of polar substance in polar solvent

Polar covalent molecule is as a whole neutral but it possesses partially positive and negative charge on its two ends. Thus when it is added into a polar solvent a   dipole–dipole interaction is developed among, solute-solvent and particles which makes it soluble.

We know that sugar is easily dissolved in water. This is due to the fact that several O – H bond in sugar molecule bear partially positive and negative charge on them. These polar areas of sugar molecule interact with positive and negative poles of water molecules to form hydrogen bonds. Due to this interaction sugar is soluble in water.

(ii) Solubility of non polar substance in polar solvent

Non polar covalent molecules do not dissolve in polar solvent. For example when benzene put into water, it does not dissolve and form two layers. The reason is that benzene is non polar whereas water is polar in nature. Thus the positive and negative poles of water behave hydrophobically with benzene and not allow to dissolving it.

(iii) Solubility of non polar substance in non polar solvent

Non polar covalent molecules dissolve in non polar solvent on the basic principle that like dissolves like due to London forces. For example oil is dissolved in hexane because both are non polar. Since interaction among the particles of both oil and hexane are weak and comparable thus on dissolution, the attractive forces of solvent are enough for overcoming the attractive forces among oil molecules hence it dissolves.

3.4.2 Reactions of Polar and Non Polar Covalent Compounds

Chemical reactions take place by the breaking of existing bonds and the formation of some new bonds. Breaking of bond requires energy. The stronger the bond in the reactant molecule the higher the energy needed for their breaking. Since the atoms in the polar covalent molecule are held more firmly, so high bond dissociation energy is required to proceed the reaction. The feasibility of a chemical reaction is determined by having the information of bond energy required to break the total number of reactant molecules and the bond energy release in bond formation in total number of product molecules.

Society, Technology and Science

Disulphide bond and Hydrogen bond in straight and curly hairs

Hairs are composed of a type of protein known as keratin. In the structure of keratin many amino acids (cystein) link to each other by permanent disulphide bonds. The distance between sulphur atoms cause hairs to curl. The greater the distance among sulphur atoms, the more keratin molecule bend and more our hair curls.

Another type of connection among neighbors' amino acid chains is hydrogen bond which is much weaker and temporary. This hydrogen bond is affected by water. In humid day, moisture of atmosphere breaks hydrogen bond of hair and makes the hair ruin.

Activity

This activity will enable you to understand the solubility of a liquid in another liquid. Take two test tubes and put few drops of cooking oil in both of them. Now add water in first test tube and petrol in the second one and shake both of them vigorously. You'll find that oil doesn't dissolve in water but in petrol it does. The reason is that oil is a non-polar organic liquid; it doesn't dissolve in water since it is polar in nature while it dissolves in petrol due to its non-polar nature.

SUMMARY with Key Terms

◆ **Valence Bond Theory** tells that covalent bond is formed by the overlapping of atomic orbital in which the shared pair of electron is localized between the two nuclei.

◆ **Molecular orbital theory** tells that when two atomic orbitals combine to form two molecular orbitals. One molecular orbital has lower energy than other orbital and known as bonding M.O. Other molecular orbital has higher energy than atomic orbital and known as anti bonding M.O.

◆ **Sigma bond** is formed by head to head overlapping of atomic orbital. It exists in s-s, s-p, p-p etc.

◆ **pi bond** is formed by the side way overlapping of atomic orbital (py-py and pz-pz). It is relatively weaker than sigma bond.

◆ **Hybridization** is the mixing of atomic orbital to produce equal number of same energy orbitals. It is of various type such as sp^3, sp^2, sp etc depending upon the number and type of orbital involved in the mixing.

◆ **Electron pair repulsion theory** describe the shape of simple covalent molecules on the basis of number of active electron pairs around the central atom.

◆ **Dipole moment** is the product of charge and the distance between positive and negative centers. It is measured in Debye, however its SI unit is coulomb meter.

◆ **Bond length** is the distance between the nuclei of two bonded atoms in a molecule. It is measured in Angstrom (Å).

◆ **Bond energy** is the amount of energy required to break 1 mole of a particular type of bond in the molecule. It is measured in KJ/mol.

◆ **Ionic character** of covalent bond is the polarity of molecule produced when the electron of two unlike atoms are shared up.

Multiple Choice Questions

1. Choose the correct answer

(i) If the bond angle in AB_2 type molecule is 104.5°, it geometry should be:
(a) Linear   (b) Pyramidal   (c) Bent   (d) Planar Trigonal

(ii) The highest bond energy in the following is:
(a) Cl – Cl   (b) H – F   (c) H – O   (d) H – N

(iii) The molecule which has zero dipole moment is:
(a) NH_3 (b) HCl   (c) H_2O (d) CCl_4

(iv) The molecule which has maximum bond angle:
(a) CS_2 (b) H_2O (c) NH_3 (d) BF_3

(v) The shape and hybridization of BCl_3 molecule is:
(a) Tetrahedral and sp^3 (b) Linear and sp
(c) Planar trigonal and sp^2 (d) Angular and sp^3

(vi) Amongst the following molecules which one has trigonal pyramidal shape?
(a) SO_2 (b) CO_2 (c) NH_3 (d) C_2H_4

(vii) A simple covalent molecule possesses two bond pairs and two lone pairs around the central atom, its shape should be:
(a) Linear   (b) Planar trigonal   (c) Angular   (d) Tetrahedral

(viii) The correct relation between Debye and coulomb meter is:
(a) $1D = 3.33 \times 10^{-30}$ Cm   (b) $1D = 1.6 \times 10^{-19}$ Cm
(c) $1D = 1.88 \times 10^{-12}$ Cm   (d) $1D = 1.23 \times 10^{-8}$ Cm

(ix) The bond order of N_2 molecule is:
(a) 0   (b) 1   (c) 2   (d) 3

(x) The number of sigma and pi bonds in C_2H_4 molecule are respectively:
(a) 3 and 1   (b) 2 and 2   (c) 5 and 1   (d) 4 and 2

1. Define the following:
   (i) Bond Energy   (ii) Bond length

2. The Dipole moment of water is 1.85D but CO_2 has zero dipole moment why?

3. Differentiate between the following:
   (i)   VBT and MOT
   (ii)   Sigma bond and pi bond
   (iii)   Bonding M.O and Anti bonding M.O

4. Explain the following with scientific reasons.
   (i)   Sigma bond is stronger than pi bond.
   (ii)   HF has greater ionic character than HCl.
   (iii)   Bond energy of molecules possessing multiple bonds is high.

5. Oil is insoluble in water but soluble in hexane explain why?

6. Which hybridization would you expect for the central atom in each of the following?
   $BeCl_2$, BF_3, CH_4, C_2H_2

Descriptive Questions

1. (a) Write down the postulate of VSEPR theory
   (b) Predict the shape of following molecules on the basis of VSEPR theory.
   $AlCl_3$, CCl_4, PH_3, H_2S

2. What do you mean by Hybridization? Explain sp^3 hybridization in CH_4 molecule and sp^2 hybridization in C_2H_4 molecule.

3. What are the basic postulates of valence bond theory? Explain various type of overlapping lead to sigma and pi bond.

4. Draw a molecular orbital diagram of O_2 molecule and
   (i)   Write down MO electronic configuration
   (ii)   Determine bond order
   (iii)   Explain the paramagnetic behavior