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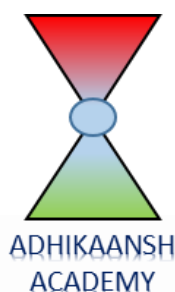
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## CHAPTER-4

### CHEMICAL BONDING AND MOLECULAR STRUCTURE

**OCTET RULE-** During a chemical reaction the atoms tend to adjust their electronic arrangement in such a way that they achieve 8 e<sup>-</sup> in their outermost electron. This is called octet rule.

**CHEMICAL BOND-** the chemical force which keeps the atoms in any molecule together is called a chemical bond.

**IONIC BOND-** The columbic force of attraction which holds the appositively charged ions together is called an ionic bond. An ionic bond is formed by the complete transfer of one or more electrons from the atom of a metal to an atom of non- metal.

**LATTICE ENTHALPY-** The molar enthalpy change accompanying the complete separation of the constituent particles that compose of the solids (such as ions for ionic solid, molecules for molecular solids) under standard conditions is called lattice enthalpy ( $\Delta_l H^\circ$ ). The lattice enthalpy is a positive quantity.

**ELECTRO VALENCY:** The number of electrons lost or gain by an atom of an element is called as electrovalency.

The element which give up electrons to form positive ions are said to have positive valency, while the elements which accept electrons to form negative ions are said to have negative valency.

**FORMATION OF AN IONIC BOND:** It is favoured by, (i) the low ionisation enthalpy of a metallic element which forms the cations, (ii) High electron gain enthalpy of non- metallic element which forms the anions, (iii) Large lattice enthalpy i.e; the smaller size and the higher charge of the atoms.

**COVALENCY:**The number of electrons which an atom contributes towards mutual sharing during the formation of a chemical bond called its covalency in that compound.

**SINGLE COVALENT BOND:** A covalent bond formed by the mutual sharing of one pair of electrons is called a single covalent bond, or simply a single bond. A single covalent bond is represented by a small line (—) between the two atoms.

**DOUBLE COVALENT BOND:** A covalent bond formed by the mutual sharing of two pair of electrons is called a double covalent bond, or simply a double bond. A double covalent bond is represented by two small horizontal lines (=) between the two atoms. E.g. O=O, O=C=O etc.

**TRIPLE COVALENT BOND:** A covalent bond formed by the mutual sharing of three pair of electrons is called a triple covalent bond, or simply a triple bond. A triple covalent bond is represented by three small horizontal lines ( $\equiv$ ) between the two atoms. E.g. N $\equiv$ N, H-C $\equiv$ C-H etc.

**FORMATION OF A COVALENT BOND:** Formation of a covalent bond is favoured by

- (i) High ionisation enthalpy of the combining elements.
- (ii) Nearly equal electron gain enthalpy and equal electro-negativities of combining elements.
- (iii) High nuclear charge and small atomic size of the combining elements.

**POLAR COVALENT BOND:** The bond between two unlike atoms which differ in their affinities for electrons is said to be polar covalent bond. E.g. H-Cl

**COORDINATE BOND:** The bond formed when one sided sharing of electrons take place is called a coordinate bond. Such a bond is also known as dative bond. It is represented by an arrow ( $\rightarrow$ ) pointing towards the acceptor atom. E.g. H<sub>3</sub>N $\rightarrow$ BF<sub>3</sub>

**Bond Length:** Bond length is defined as the equilibrium distance between the nuclei of two bonded atoms in a molecule

**Bond Angle:** It is defined as the angle between the orbitals containing bonding electron pairs around the central atom in a molecule/complex ion

**Bond Enthalpy:** It is defined as the amount of energy required to break one mole of bonds of a particular type between two atoms in a gaseous state.

**Bond Order:** In the Lewis description of covalent bond, the Bond Order is given by the number of




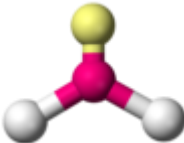
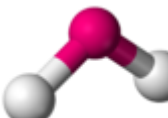

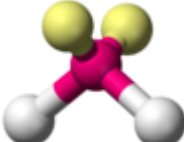
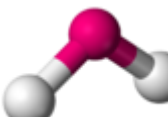
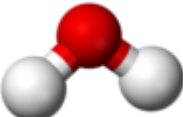
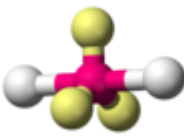
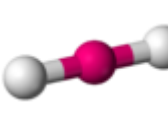
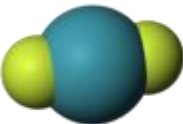
**SIGMA BOND:** A covalent bond formed due to the overlapping of orbitals of the two atoms along the line joining the two nuclei (orbital axis) is called sigma ( $\sigma$ ) bond. For example, the bond formed due to s-s and s-p, p-p overlapping along the orbital axis are sigma bonds.

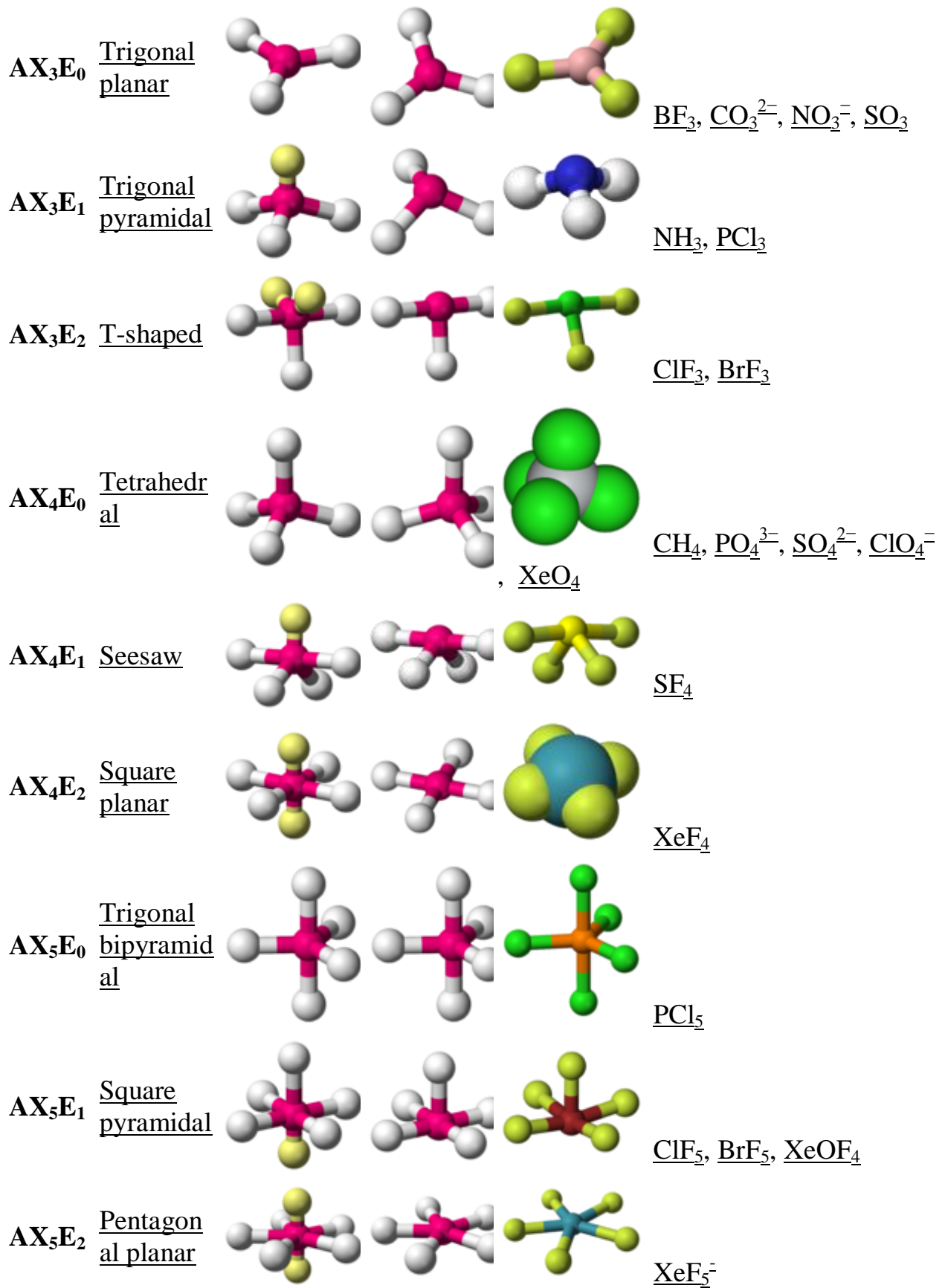
**Pi- BOND:** A covalent bond formed by the side wise overlapping of p- or d- orbitals of two atoms is called as pi ( $\pi$ ) bond. For example, the bond formed due to the sideways overlapping of the two p- orbitals is a pi- bond.

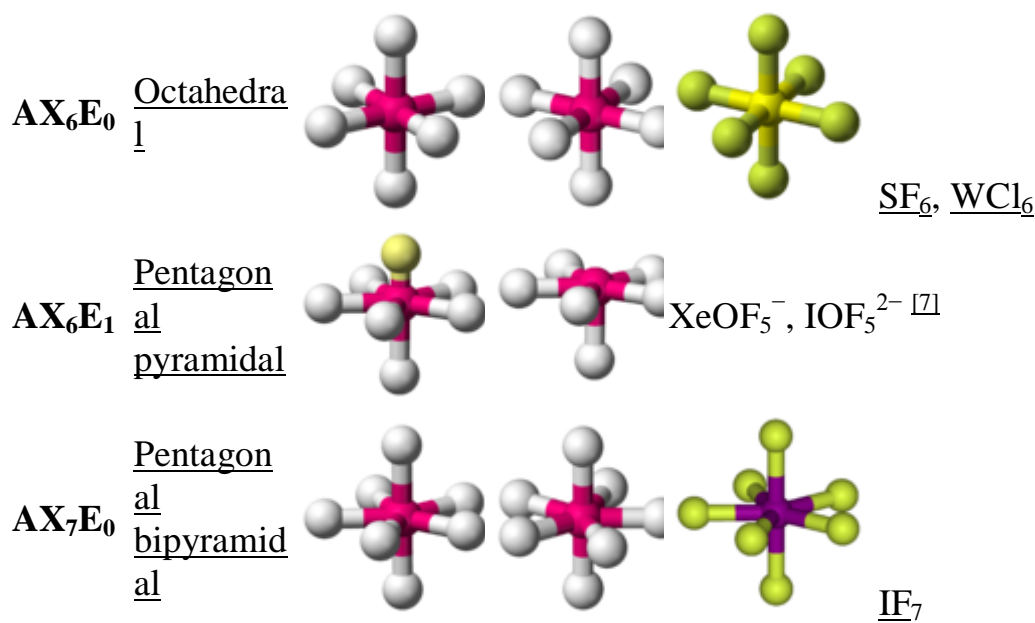
**HYDROGEN BOND:** The bond between the hydrogen atom of one molecule and a more electro- negative element of same or another molecule is called as hydrogen bond.

**HYBRIDIZATION:** The process of mixing of the atomic orbitals to form new hybrid orbitals is called hybridization. All hybrid orbitals of a particular kind have equal energy, identical shapes and are symmetrically oriented in shape.

The hybrid orbitals are designed according to the type and the atomic orbitals merging together, e.g.,

Molecule Type	Shape	Electron arrangement <sup>†</sup>	Geometry <sup>‡</sup>	Examples	
$AX_2E_0$	<u>Linear</u>				<u>BeCl<sub>2</sub></u> , <u>HgCl<sub>2</sub></u> , <u>CO<sub>2</sub></u>
$AX_2E_1$	<u>Bent</u>				<u>NO<sub>2</sub><sup>-</sup></u> , <u>SO<sub>2</sub></u> , <u>O<sub>3</sub></u> , <u>CCl<sub>2</sub></u>
$AX_2E_2$	<u>Bent</u>				<u>H<sub>2</sub>O</u> , <u>OF<sub>2</sub></u>
$AX_2E_3$	<u>Linear</u>				<u>XeF<sub>2</sub></u> , <u>I<sub>3</sub><sup>-</sup></u> , <u>XeCl<sub>2</sub></u>





**ONE MARK QUESTIONS**

Q.1. What is the total number of sigma and pi bonds in the following molecules?

- (a)  $\text{C}_2\text{H}_2$  (b)  $\text{C}_2\text{H}_4$

Ans- there are three sigma and two pi-bonds in  $\text{C}_2\text{H}_2$ .

there are five sigma bonds and one pi-bond in  $\text{C}_2\text{H}_4$ .

Q.2. Write the significance of a plus and a minus sign shown in representing the orbitals.

Ans- Molecular orbitals are represented by wave functions. A plus sign in an orbital indicates a positive wave function while a minus sign in an orbital represents a negative wave function.

Q.3. How do you express the bond strength in terms of bond order?

Ans- Bond strength represents the extent of bonding between two atoms forming a molecule. The larger the bond energy, the stronger is the bond and the greater is the bond order.

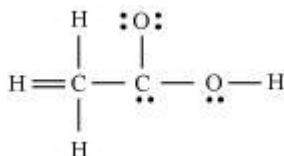
Q.5. Define the bond length.

Ans- Bond length is defined as the equilibrium distance between the nuclei of two bonded atoms in a molecule.

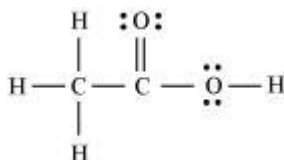
Q.6. Arrange the bonds in order of increasing ionic character in the molecules: LiF, K<sub>2</sub>O, N<sub>2</sub>, SO<sub>2</sub> and ClF<sub>3</sub>.

Ans- N<sub>2</sub> < SO<sub>2</sub> < ClF<sub>3</sub> < K<sub>2</sub>O < LiF.

Q.7. The skeletal structure of CH<sub>3</sub>COOH as shown below is correct, but some of the bonds are shown incorrectly. Write the correct Lewis structure for acetic acid.



Ans- The correct Lewis structure for acetic acid is as follows:



Q.8. Define octet rule.

Ans- The elements tend to adjust the arrangement of their electrons in such a way that they (except H and He) achieve eight electrons in their outermost shell. This is called octet rule.

Q.9. Define lattice enthalpy.

Ans- The energy required when one mole of an ionic compound in crystalline form is split into the constituent ions is called lattice enthalpy.

Q.10. Which type of bond is formed when the atoms have zero difference in electronegativity?

Ans- Covalent bond.

## TWO MARKS QUESTIONS

Q.1. Define hydrogen bond. Is it weaker or stronger than the van der Waals forces?

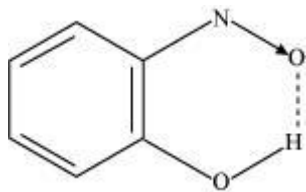
Ans- A hydrogen bond is defined as an attractive force acting between the hydrogen attached to an electronegative atom of one molecule and an electronegative atom of a different molecule (may be of the same kind).

There are two types of H-bonds:



(i) Intermolecular H-bond e.g., HF, H<sub>2</sub>O etc.

(ii) Intramolecular H-bond e.g., o-nitrophenol



Hydrogen bonds are stronger than Van der Waals forces since hydrogen bonds are regarded as an extreme form of dipole-dipole interaction.

Q.2. Write the favourable factors for the formation of ionic bond.

Ans-(i) Low ionization enthalpy of metal atom.

(ii) High electron gain enthalpy ( $\Delta_{eg} H$ ) of a non-metal atom.

(iii) High lattice energy of the compound formed.

Q.3. Although geometries of NH<sub>3</sub> and H<sub>2</sub>O molecules are distorted tetrahedral, bond angle in water is less than that of ammonia. Discuss.

Ans- The molecular geometry of NH<sub>3</sub> and H<sub>2</sub>O can be shown as:



The central atom (N) in NH<sub>3</sub> has one lone pair and there are three bond pairs. In H<sub>2</sub>O, there are two lone pairs and two bond pairs.

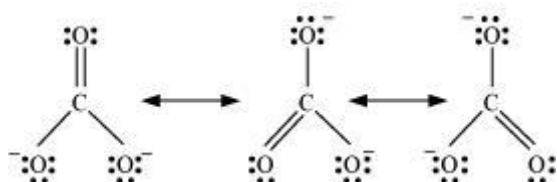
The two lone pairs present in the oxygen atom of H<sub>2</sub>O molecule repels the two bond pairs. This repulsion is stronger than the repulsion between the lone pair and the three bond pairs on the nitrogen atom.

Since the repulsions on the bond pairs in H<sub>2</sub>O molecule are greater than that in NH<sub>3</sub>, the bond angle in water is less than that of ammonia.

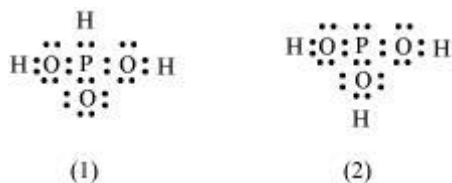
Q.4. Explain the important aspects of resonance with reference to the CO<sub>3</sub><sup>2-</sup> ion.

Ans- According to experimental findings, all carbon to oxygen bonds in  $\text{CO}_3^{2-}$  are equivalent. Hence, it is inadequate to represent  $\text{CO}_3^{2-}$  ion by a single Lewis structure having two single bonds and one double bond.

Therefore, carbonate ion is described as a resonance hybrid of the following structures:



Q.5.  $\text{H}_3\text{PO}_3$  can be represented by structures 1 and 2 shown below. Can these two structures be taken as the canonical forms of the resonance hybrid representing  $\text{H}_3\text{PO}_3$ ? If not, give reasons for the same.



Ans- The given structures cannot be taken as the canonical forms of the resonance hybrid of  $\text{H}_3\text{PO}_3$  because the positions of the atoms have changed.

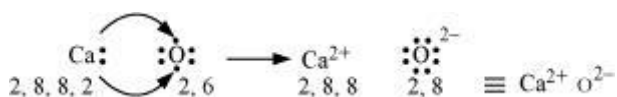
Q.6. Use Lewis symbols to show electron transfer between the following atoms to form cations and anions: (a) Ca and O (c) Al and N.

Ans(a) Ca and O:

The electronic configurations of Ca and O are as follows:

Ca: 2, 8, 8, 2            O: 2, 6

Oxygen requires two electrons more to complete its octet, whereas calcium has two electrons more than the nearest noble gas i.e., Argon. Hence, the electron transfer takes place as:

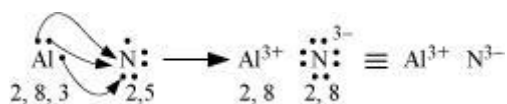


(b) Al and N:

The electronic configurations of Al and N are as follows:

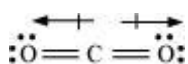
Al: 2, 8, 3            N: 2, 5

Nitrogen is three electrons short of the nearest noble gas (Neon), whereas aluminium has three electrons more than Neon. Hence, the electron transference can be shown as:



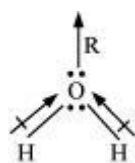
Q.7. Although both CO<sub>2</sub> and H<sub>2</sub>O are triatomic molecules, the shape of H<sub>2</sub>O molecule is bent while that of CO<sub>2</sub> is linear. Explain this on the basis of dipole moment.

Ans- According to experimental results, the dipole moment of carbon dioxide is zero. This is possible only if the molecule is linear so that the dipole moments of C–O bonds are equal and opposite to nullify each other.



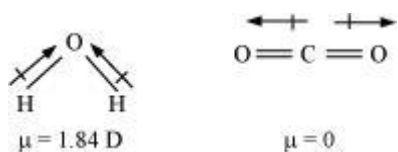
Resultant  $\mu = 0$  D

H<sub>2</sub>O, on the other hand, has a dipole moment value of 1.84 D (though it is a triatomic molecule as CO<sub>2</sub>). The value of the dipole moment suggests that the structure of H<sub>2</sub>O molecule is bent where the dipole moment of O–H bonds are unequal.



Q.8. Write the significance/applications of dipole moment.

Ans- Dipole moment is the measure of the polarity of a bond. It is used to differentiate between polar and non-polar bonds since all non-polar molecules (e.g. H<sub>2</sub>, O<sub>2</sub>) have zero dipole moments. It is also helpful in calculating the percentage ionic character of a molecule.



Q.9. Use molecular orbital theory to explain why the  $\text{Be}_2$  molecule does not exist.

Ans- The electronic configuration of Beryllium is  $1s^2 2s^2$ .

The molecular orbital electronic configuration for  $\text{Be}_2$  molecule can be written as:

$$\begin{array}{cccc} \sigma_{1s}^2 & \sigma_{1s}^{*2} & \sigma_{2s}^2 & \sigma_{2s}^{*2} \end{array} \quad \text{Hence, the bond order for } \text{Be}_2 \text{ is } \frac{1}{2}(N_b - N_a).$$

Where,

$N_b$  = Number of electrons in bonding orbitals

$N_a$  = Number of electrons in anti-bonding orbitals

$$\therefore \text{Bond order of } \text{Be}_2 = \frac{1}{2}(4-4) = 0$$

A negative or zero bond order means that the molecule is unstable.

Hence,  $\text{Be}_2$  molecule does not exist.

Q.10. Distinguish between a sigma and a pi bond.

Ans- The following are the differences between sigma and pi-bonds:

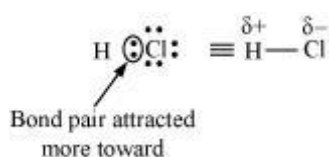
<b>Sigma (<math>\sigma</math>) Bond</b>	<b>Pi (<math>\pi</math>) Bond</b>
(a) It is formed by the end to end overlap of orbitals.	It is formed by the lateral overlap of orbitals.
(b) The orbitals involved in the overlapping are $s-s$ , $s-p$ , or $p-p$ .	These bonds are formed by the overlap of $p-p$ orbitals only.
(c) It is a strong bond.	It is weak bond.
(d) The electron cloud is symmetrical about the line joining the two nuclei.	The electron cloud is not symmetrical.
(e) It consists of one electron cloud, which is symmetrical about the internuclear axis.	There are two electron clouds lying above and below the plane of the atomic nuclei.
(f) Free rotation about $\sigma$ bonds is possible.	Rotation is restricted in case of pi-bonds.

Q.11. Explain with the help of suitable example polar covalent bond.

Ans- When two dissimilar atoms having different electronegativities combine to form a covalent bond, the bond pair of electrons is not shared equally. The bond pair shifts towards the nucleus of the atom having greater electronegativity. As a result, electron distribution gets distorted and the electron cloud is displaced towards the electronegative atom.

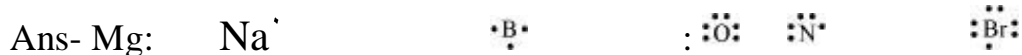
As a result, the electronegative atom becomes slightly negatively charged while the other atom becomes slightly positively charged. Thus, opposite poles are developed in the molecule and this type of a bond is called a polar covalent bond.

HCl, for example, contains a polar covalent bond. Chlorine atom is more electronegative than hydrogen atom. Hence, the bond pair lies towards chlorine and therefore, it acquires a partial negative charge.



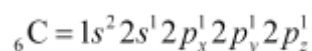
### THREE MARKS QUESTIONS

Q.1. Write Lewis dot symbols for atoms of the following elements: Mg, Na, B, O, N, Br.

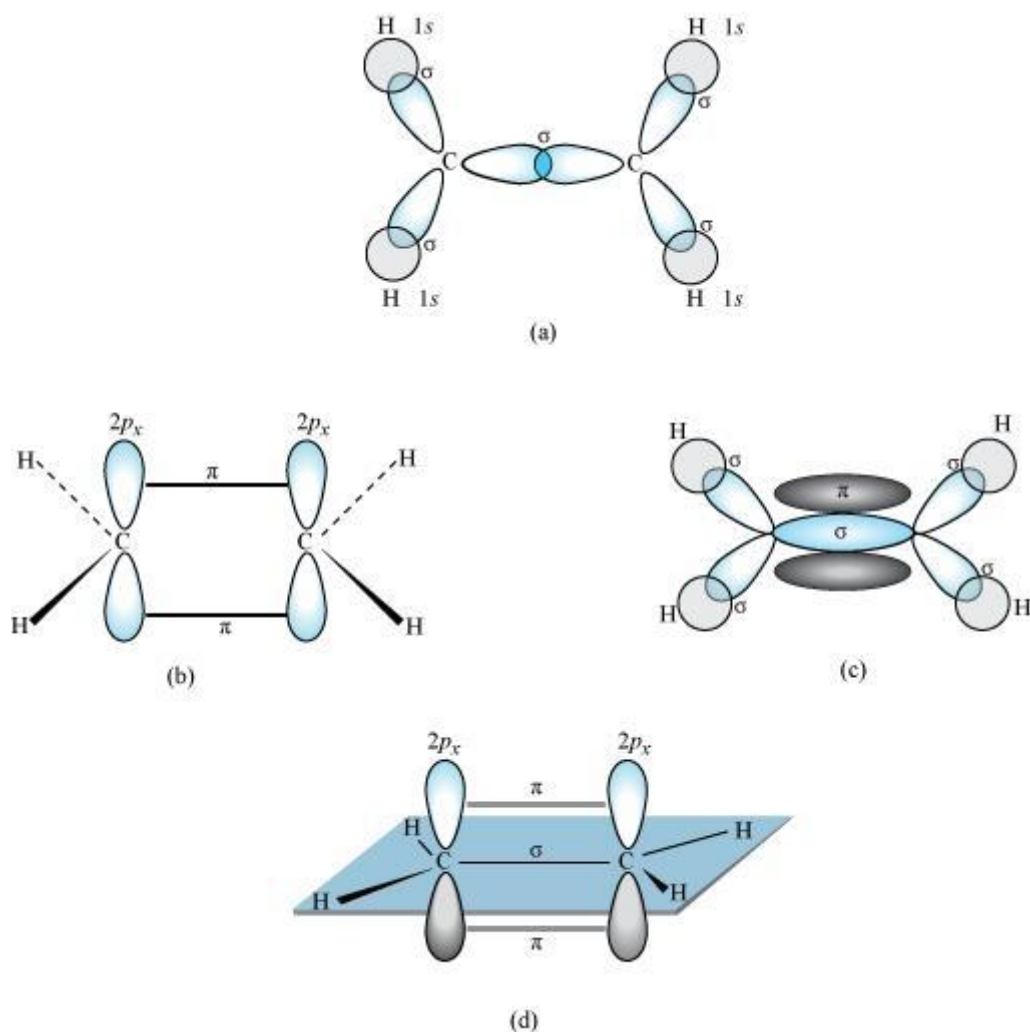


Q.3. Draw diagrams showing the formation of a double bond and a triple bond between carbon atoms in C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>2</sub> molecules.

Ans- **C<sub>2</sub>H<sub>4</sub>**: The electronic configuration of C-atom in the excited state is:



In the formation of an ethane molecule (C<sub>2</sub>H<sub>4</sub>), one *sp*<sup>2</sup> hybrid orbital of carbon overlaps a *sp*<sup>2</sup> hybridized orbital of another carbon atom, thereby forming a C-C sigma bond. The remaining two *sp*<sup>2</sup> orbitals of each carbon atom form a *sp*<sup>2</sup>-s sigma bond with two hydrogen atoms. The unhybridized orbital of one carbon atom undergoes sidewise overlap with the orbital of a similar kind present on another carbon atom to form a weak π-bond.

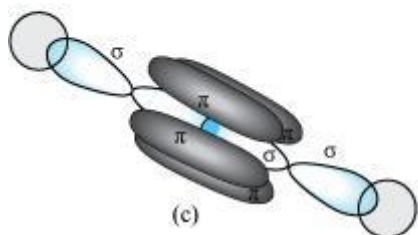
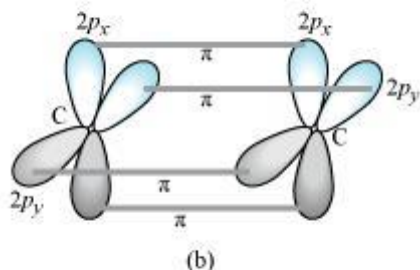
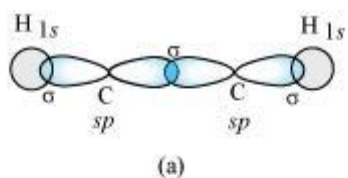


### $C_2H_2$ :

In the formation of  $C_2H_2$  molecule, each C-atom is  $sp$  hybridized with two  $2p$ -orbitals in an unhybridized state.

One  $sp$  orbital of each carbon atom overlaps with the other along the internuclear axis forming a C–C sigma bond. The second  $sp$  orbital of each C-atom overlaps a half-filled  $1s$ -orbital to form a  $\sigma$  bond.

The two unhybridized  $2p$ -orbitals of the first carbon undergo sidewise overlap with the  $2p$  orbital of another carbon atom, thereby forming two pi ( $\pi$ ) bonds between carbon atoms. Hence, the triple bond between two carbon atoms is made up of one sigma and two  $\pi$ -bonds.



Q.4. Explain the formation of  $H_2$  molecule on the basis of valence bond theory.

Ans- Let us assume that two hydrogen atoms (A and B) with nuclei ( $N_A$  and  $N_B$ ) and electrons ( $e_A$  and  $e_B$ ) are taken to undergo a reaction to form a hydrogen molecule. When A and B are at a large distance, there is no interaction between them. As they begin to approach each other, the attractive and repulsive forces start operating.

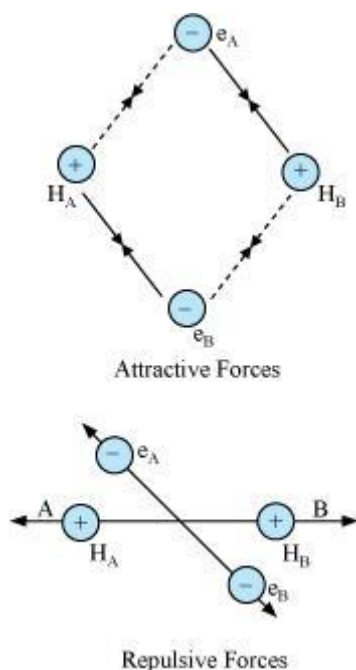
Attractive force arises between:

- (a) Nucleus of one atom and its own electron i.e.,  $N_A - e_A$  and  $N_B - e_B$ .
- (b) Nucleus of one atom and electron of another atom i.e.,  $N_A - e_B$  and  $N_B - e_A$ .

Repulsive force arises between:

- (a) Electrons of two atoms i.e.,  $e_A - e_B$ .
- (b) Nuclei of two atoms i.e.,  $N_A - N_B$ .

The force of attraction brings the two atoms together, whereas the force of repulsion tends to push them apart.



The magnitude of the attractive forces is more than that of the repulsive forces. Hence, the two atoms approach each other. As a result, the potential energy decreases. Finally, a state is reached when the attractive forces balance the repulsive forces and the system acquires minimum energy. This leads to the formation of a dihydrogen molecule.

Q.5. Write the important conditions required for the linear combination of atomic orbitals to form molecular orbitals.

Ans- The given conditions should be satisfied by atomic orbitals to form molecular orbitals:

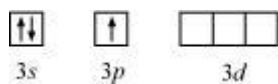
- The combining atomic orbitals must have the same or nearly the same energy. This means that in a homonuclear molecule, the  $1s$ -atomic orbital of an atom can combine with the  $1s$ -atomic orbital of another atom, and not with the  $2s$ -orbital.
- The combining atomic orbitals must have proper orientations to ensure that the overlap is maximum.
- The extent of overlapping should be large.

Q.6. Describe the hybridisation in case of  $PCl_5$ . Why are the axial bonds longer as compared to equatorial bonds?

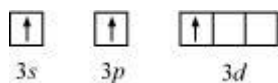
Ans- The ground state and excited state outer electronic configurations of phosphorus ( $Z = 15$ ) are:

Ground state:



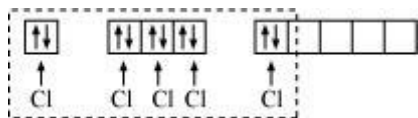


Excited state:

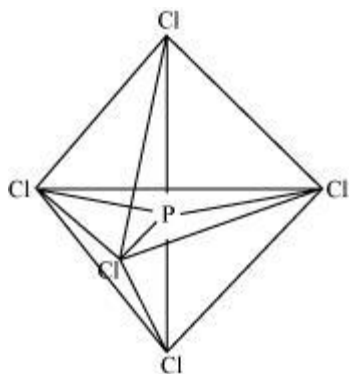


Phosphorus atom is  $sp^3d$  hybridized in the excited state. These orbitals are filled by the electron pairs donated by five Cl atoms as:

$PCl_5$



The five  $sp^3d$  hybrid orbitals are directed towards the five corners of the trigonal bipyramidals. Hence, the geometry of  $PCl_5$  can be represented as:



There are five P–Cl sigma bonds in  $PCl_5$ . Three P–Cl bonds lie in one plane and make an angle of  $120^\circ$  with each other. These bonds are called equatorial bonds. The remaining two P–Cl bonds lie above and below the equatorial plane and make an angle of  $90^\circ$  with the plane. These bonds are called axial bonds. As the axial bond pairs suffer more repulsion from the equatorial bond pairs, axial bonds are slightly longer than equatorial bonds.

Q.7. What is meant by the term bond order? Calculate the bond order of:  $N_2$ ,  $O_2$ ,  $O_2^+$  and  $O_2^-$ .

Ans- Bond order is defined as one half of the difference between the number of electrons present in the bonding and anti-bonding orbitals of a molecule.

$$\text{Bond order} = \frac{1}{2}(N_b - N_a)$$

Bond order of  $N_2$

$$[\sigma(1s)]^2[\sigma^*(1s)]^2[\sigma(2s)]^2[\sigma^*(2s)]^2[\pi(2p_x)]^2[\pi(2p_y)]^2[\sigma(2p_z)]^2$$

Number of bonding electrons,  $N_b = 10$

Number of anti-bonding electrons,  $N_a = 4$

$$\text{Bond order of nitrogen molecule} = \frac{1}{2}(10 - 4) = 3$$

Bond order of  $O_2$

$$[\sigma(1s)]^2[\sigma^*(1s)]^2[\sigma(2s)]^2[\sigma^*(2s)]^2[\sigma(2p_z)]^2[\pi(2p_x)]^2[\pi(2p_y)]^2[\pi^*(2p_x)]^1[\pi^*(2p_y)]^1$$

$$\text{Bond order} = \frac{1}{2}(N_b - N_a) = \frac{1}{2}(8 - 4) = 2$$

Hence, the bond order of oxygen molecule is 2.

Similarly, the electronic configuration of  $O_2^+$  can be written as:

$$KK[\sigma(2s)]^2[\sigma^*(2s)]^2[\sigma(2p_z)]^2[\pi(2p_x)]^2[\pi(2p_y)]^2[\pi^*(2p_x)]^1$$

$$\text{Bond order of } O_2^+ = \frac{1}{2}(8 - 3) = 2.5$$

The electronic configuration of  $O_2^-$  ion will be:

$$KK[\sigma(2s)]^2[\sigma^*(2s)]^2[\sigma(2p_z)]^2[\pi(2p_x)]^2[\pi(2p_y)]^2[\pi^*(2p_x)]^2[\pi^*(2p_y)]^1$$

$$\text{Bond order of } O_2^- = \frac{1}{2}(8 - 5) = 1.5$$

Q.8. Discuss the shape of the following molecules using the VSEPR model:

$BeCl_2$ ,  $BCl_3$ ,  $SiCl_4$ ,  $AsF_5$ ,  $H_2S$ ,  $PH_3$

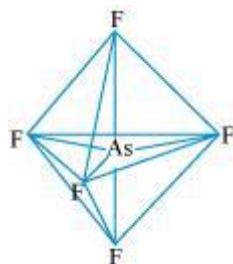
Ans-  $BeCl_2$ :  $Cl:Be:Cl$  The central atom has no lone pair and there are two bond pairs. i.e.,  $BeCl_2$  is of the type  $AB_2$ . Hence, it has a linear shape.

BCl<sub>3</sub>:  $\begin{array}{c} \text{Cl} \\ \vdots \\ \text{Cl} : \text{B} : \text{Cl} \\ \vdots \end{array}$  The central atom has no lone pair and there are three bond pairs.

Hence, it is of the type AB<sub>3</sub>. Hence, it is trigonal planar.



SiCl<sub>4</sub>:  $\begin{array}{c} \text{Cl} \\ \vdots \\ \text{Cl} : \text{Si} : \text{Cl} \\ \vdots \\ \text{Cl} \end{array}$  The central atom has no lone pair and there are four bond pairs. Hence, the shape of SiCl<sub>4</sub> is tetrahedral being the AB<sub>4</sub> type molecule.



AsF<sub>5</sub>: The central atom has no lone pair and there are five bond pairs. Hence, AsF<sub>5</sub> is of the type AB<sub>5</sub>. Therefore, the shape is trigonal bipyramidal.

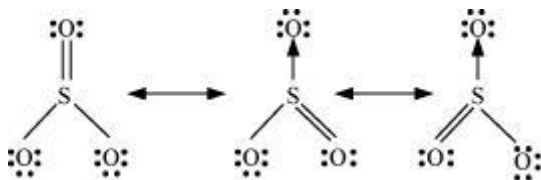
H<sub>2</sub>S:  $\begin{array}{c} \vdots \\ \text{H} : \text{S} : \text{H} \\ \vdots \end{array}$  The central atom has one lone pair and there are two bond pairs. Hence, H<sub>2</sub>S is of the type AB<sub>2</sub>E. The shape is Bent.

PH<sub>3</sub>:  $\begin{array}{c} \vdots \\ \text{H} : \text{P} : \text{H} \\ \vdots \\ \text{H} \end{array}$  The central atom has one lone pair and there are three bond pairs. Hence, PH<sub>3</sub> is of the AB<sub>3</sub>E type. Therefore, the shape is trigonal bipyramidal.

Q.9. Write the resonance structures for SO<sub>3</sub>, NO<sub>2</sub> and NO<sub>3</sub><sup>-</sup>.

Ans- The resonance structures are:

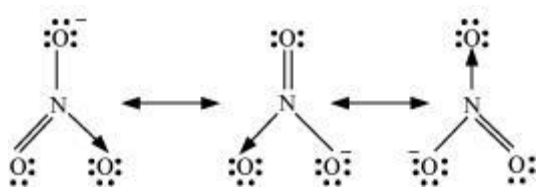
(a) SO<sub>3</sub>:



(b) NO<sub>2</sub>:



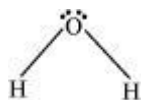
(c)  $\text{NO}_3^-$ :



Q.10. What do you understand by bond pairs and lone pairs of electrons? Illustrate by giving example.

Ans- The shared pairs of electrons present between the bonded atoms are called **bond pairs**. All valence electrons may not participate in bonding. The electron pairs that do not participate in bonding are called **lone pairs** of electrons.

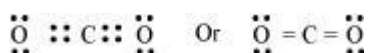
In  $\text{H}_2\text{O}$ , there are two bond pairs and two lone pairs on the central atom (oxygen).



### FIVE MARKS QUESTIONS

Q.1. Define octet rule. Write its significance and limitations.

Ans-- The octet rule or the electronic theory of chemical bonding was developed by Kossel and Lewis. According to this rule, atoms can combine either by transfer of valence electrons from one atom to another or by sharing their valence electrons in order to attain the nearest noble gas configuration by having an octet in their valence shell.



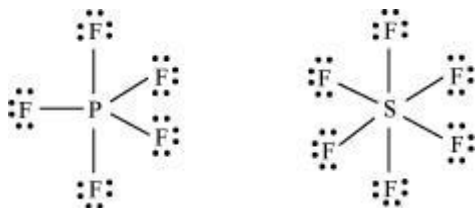
The octet rule successfully explained the formation of chemical bonds depending upon the nature of the element.

Limitations of the octet theory:

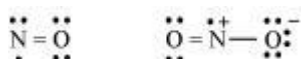
The following are the limitations of the octet rule:

- The rule failed to predict the shape and relative stability of molecules.
- It is based upon the inert nature of noble gases. However, some noble gases like xenon and krypton form compounds such as  $\text{XeF}_2$ ,  $\text{KrF}_2$  etc.

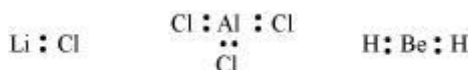
(c) The octet rule cannot be applied to the elements in and beyond the third period of the periodic table. The elements present in these periods have more than eight valence electrons around the central atom. For example:  $\text{PF}_5$ ,  $\text{SF}_6$ , etc.



(d) The octet rule is not satisfied for all atoms in a molecule having an odd number of electrons. For example,  $\text{NO}$  and  $\text{NO}_2$  do not satisfy the octet rule.



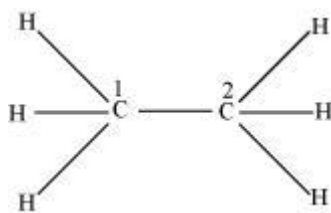
(e) This rule cannot be applied to those compounds in which the number of electrons surrounding the central atom is less than eight. For example,  $\text{LiCl}$ ,  $\text{BeH}_2$ ,  $\text{AlCl}_3$  etc. do not obey the octet rule.



Q.2. Which hybrid orbitals are used by carbon atoms in the following molecules?

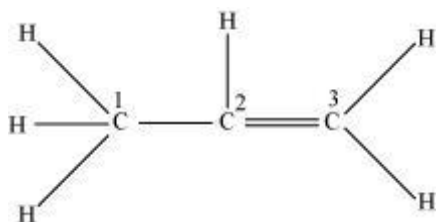
$\text{CH}_3\text{-CH}_3$ ; (b)  $\text{CH}_3\text{-CH=CH}_2$ ; (c)  $\text{CH}_3\text{-CH}_2\text{-OH}$ ; (d)  $\text{CH}_3\text{-CHO}$  (e)  $\text{CH}_3\text{COOH}$

Ans- (a)



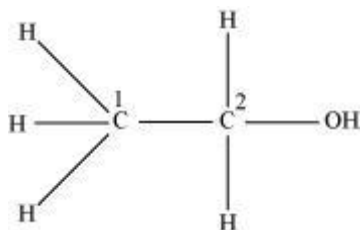
Both  $\text{C}_1$  and  $\text{C}_2$  are  $sp^3$  hybridized.

(b)



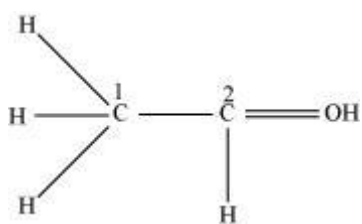
$C_1$  is  $sp^3$  hybridized, while  $C_2$  and  $C_3$  are  $sp^2$  hybridized.

(c)



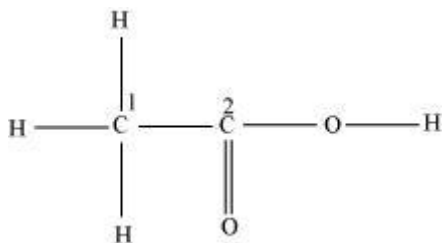
Both  $C_1$  and  $C_2$  are  $sp^3$  hybridized.

(d)



$C_1$  is  $sp^3$  hybridized and  $C_2$  is  $sp^2$  hybridized.

(e)

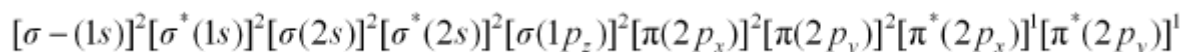


$C_1$  is  $sp^3$  hybridized and  $C_2$  is  $sp^2$  hybridized.

Q.3. Compare the relative stability of the following species and indicate their magnetic properties;

$O_2$ ,  $O_2^+$ ,  $O_2^-$  (superoxide),  $O_2^{2-}$  (peroxide)

Ans- There are 16 electrons in a molecule of dioxygen, 8 from each oxygen atom. The electronic configuration of oxygen molecule can be written as:



Since the 1s orbital of each oxygen atom is not involved in bonding, the number of bonding electrons = 8 =  $N_b$  and the number of anti-bonding orbitals = 4 =  $N_a$ .

$$\text{Bond order} = \frac{1}{2}(N_b - N_a)$$

$$= \frac{1}{2}(8 - 4)$$

$$= 2$$

Similarly, the electronic configuration of  $O_2^+$  can be written as:

$$KK[\sigma(2s)]^2[\sigma^*(2s)]^2[\sigma(2p_z)]^2[\pi(2p_x)]^2[\pi(2p_y)]^2[\pi^*(2p_x)]^1$$

$$N_b = 8$$

$$N_a = 3$$

$$\text{Bond order of } O_2^+ = \frac{1}{2}(8 - 3)$$

$$= 2.5$$

Electronic configuration of  $O_2^-$  ion will be:

$$KK[\sigma(2s)]^2[\sigma^*(2s)]^2[\sigma(2p_z)]^2[\pi(2p_x)]^2[\pi(2p_y)]^2[\pi^*(2p_x)]^2[\pi^*(2p_y)]^1$$

$$N_b = 8$$

$$N_a = 5$$

$$\text{Bond order of } O_2^- = \frac{1}{2}(8 - 5)$$

$$= 1.5$$

Electronic configuration of  $O_2^{2-}$  ion will be:

$$KK[\sigma(2s)]^2[\sigma^*(2s)]^2[\sigma(2p_z)]^2[\pi(2p_x)]^2[\pi(2p_y)]^2[\pi^*(2p_x)]^2[\pi^*(2p_y)]^2$$

$$N_b = 8$$

$$N_a = 6$$

$$\text{Bond order of } O_2^{2-} = \frac{1}{2}(8-6)$$

$$= 1$$

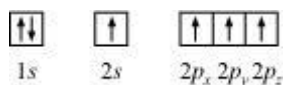
Bond dissociation energy is directly proportional to bond order. Thus, the higher the bond order, the greater will be the stability. On this basis, the order of stability is  $O_2^+ > O_2 > O_2^- > O_2^{2-}$ .

### HOTS

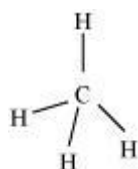
Q.1. Apart from tetrahedral geometry, another possible geometry for  $CH_4$  is square planar with the four H atoms at the corners of the square and the C atom at its centre. Explain why  $CH_4$  is not square planar?

Ans- Electronic configuration of carbon atom:  ${}_6C: 1s^2 2s^2 2p^2$

In the excited state, the orbital picture of carbon can be represented as:



Hence, carbon atom undergoes  $sp^3$  hybridization in  $CH_4$  molecule and takes a tetrahedral shape.



For a square planar shape, the hybridization of the central atom has to be  $dsp^2$ . However, an atom of carbon does not have  $d$ -orbitals to undergo  $dsp^2$  hybridization. Hence, the structure of  $CH_4$  cannot be square planar.

Moreover, with a bond angle of  $90^\circ$  in square planar, the stability of  $CH_4$  will be very less because of the repulsion existing between the bond pairs. Hence, VSEPR theory also supports a tetrahedral structure for  $CH_4$ .

Q.2. Explain why  $BeH_2$  molecule has a zero dipole moment although the Be-H bonds are polar.



Ans- The Lewis structure for  $\text{BeH}_2$  is as follows:  $\text{H}:\text{Be}:\text{H}$

There is no lone pair at the central atom (Be) and there are two bond pairs. Hence,  $\text{BeH}_2$  is of the type  $\text{AB}_2$ . It has a linear structure.

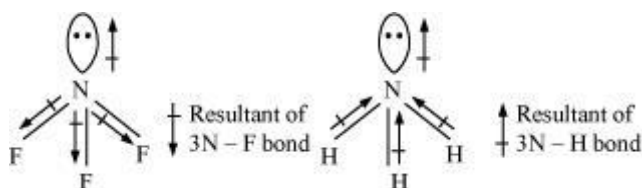


Dipole moments of each H–Be bond are equal and are in opposite directions. Therefore, they nullify each other. Hence,  $\text{BeH}_2$  molecule has zero dipole moment.

Q.3. Which out of  $\text{NH}_3$  and  $\text{NF}_3$  has higher dipole moment and why?

Ans- In both molecules i.e.,  $\text{NH}_3$  and  $\text{NF}_3$ , the central atom (N) has a lone pair electron and there are three bond pairs. Hence, both molecules have a pyramidal shape. Since fluorine is more electronegative than hydrogen, it is expected that the net dipole moment of  $\text{NF}_3$  is greater than  $\text{NH}_3$ . However, the net dipole moment of  $\text{NH}_3$  (1.46 D) is greater than that of  $\text{NF}_3$  (0.24 D).

This can be explained on the basis of the directions of the dipole moments of each individual bond in  $\text{NF}_3$  and  $\text{NH}_3$ . These directions can be shown as:



Thus, the resultant moment of the N–H bonds add up to the bond moment of the lone pair (the two being in the same direction), whereas that of the three N – F bonds partly cancels the moment of the lone pair.

Hence, the net dipole moment of  $\text{NF}_3$  is less than that of  $\text{NH}_3$ .

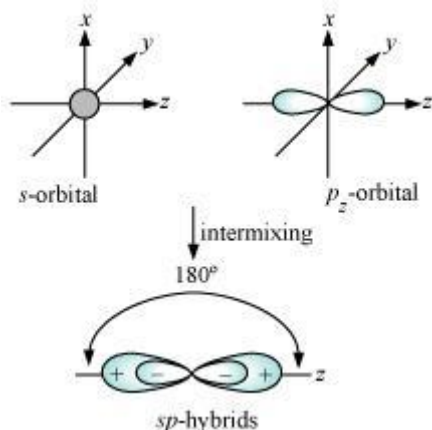
Q.4. What is meant by hybridisation of atomic orbitals? Describe the shapes of  $sp$ ,  $sp^2$ ,  $sp^3$  hybrid orbitals.

Ans- Hybridization is defined as an intermixing of a set of atomic orbitals of slightly different energies, thereby forming a new set of orbitals having equivalent energies and shapes.

For example, one  $2s$ -orbital hybridizes with two  $2p$ -orbitals of carbon to form three new  $sp^2$  hybrid orbitals.

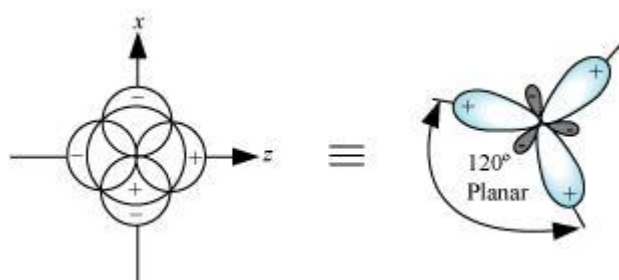
These hybrid orbitals have minimum repulsion between their electron pairs and thus, are more stable. Hybridization helps indicate the geometry of the molecule.

**Shape of  $sp$  hybrid orbitals:**  $sp$  hybrid orbitals have a linear shape. They are formed by the intermixing of  $s$  and  $p$  orbitals as:



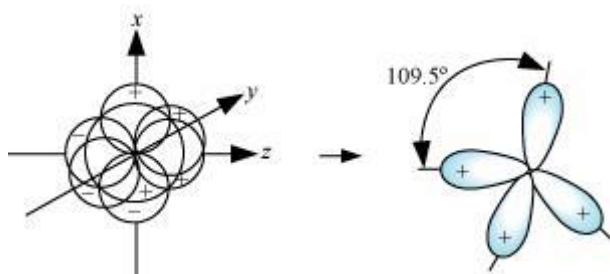
**Shape of  $sp^2$  hybrid orbitals:**

$sp^2$  hybrid orbitals are formed as a result of the intermixing of one  $s$ -orbital and two  $2p$ -orbitals. The hybrid orbitals are oriented in a trigonal planar arrangement as:



**Shape of  $sp^3$  hybrid orbitals:**

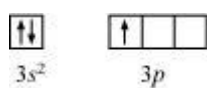
Four  $sp^3$  hybrid orbitals are formed by intermixing one  $s$ -orbital with three  $p$ -orbitals. The four  $sp^3$  hybrid orbitals are arranged in the form of a tetrahedron as:



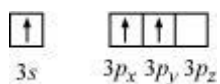
Q.5. Describe the change in hybridisation (if any) of the Al atom in the following reaction.



Ans- The valence orbital picture of aluminium in the ground state can be represented as:



The orbital picture of aluminium in the excited state can be represented as:



Hence, it undergoes  $sp^2$  hybridization to give a trigonal planar arrangement (in  $\text{AlCl}_3$ ).

To form  $\text{AlCl}_4^-$ , the empty  $3p_z$  orbital also gets involved and the hybridization changes from  $sp^2$  to  $sp^3$ . As a result, the shape gets changed to tetrahedral.

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