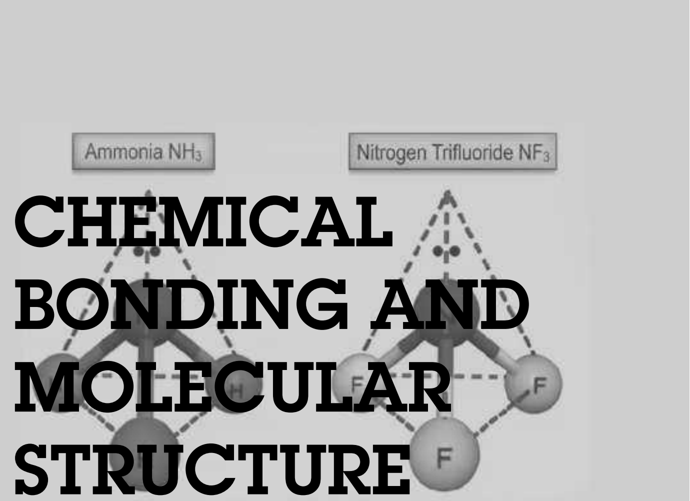
CHAPTER

4

CHEMICAL BONDING AND MOLECULAR STRUCTURE



Chapter Objectives

- *Valence electrons*
- *Chemical bond*
- *Octet rule*
- *Ionic bond*
- *Covalent bond*
- *Bond parameters*
- *Lewis structure,*
- *Polar character of covalent bond*
- *Covalent character of ionic bond,*
- *Valence bond theory,*
- *Resonance,*
- *Geometry of covalent molecules,*
- *VSEPR theory,*
- *Concept of hybridization involving s, p and d orbitals and shapes of some simple molecules*
- *Molecular orbital theory of homonuclear diatomic molecules (qualitative idea only)*
- *Hydrogen bond.*

TOPIC-1

General Introduction to Bonding : Ionic and Covalent Bonds

Quick Review

- **Chemical Bond :** The attractive force which holds together the constituent particles (atoms, ions or molecules) in a chemical species is known as chemical bond.
- **Octet Rule :** 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. The principle of attaining maximum of eight electrons in the valence shell of atoms is called octet rule.
- **Limitations of the Octet Rule :** Some limitations of octet rule are :
  - It cannot be applied to the non-metals after silicon in the periodic table.
  - These elements can “expand their octet” and have more than eight valence electrons around the central atom, e.g. PF_5, SF_6 etc.
  - Molecules with an odd number of electrons such as NO and NO_2 cannot satisfy the octet rule.

TOPIC - 1
General Introduction to Bonding :
Ionic and Covalent Bonds

TOPIC - 2
Resonance and VSEPR Theory

TOPIC - 3
Valence Bond Theory, Hybridisation,
Molecular Orbital Theory and
Hydrogen Bonding

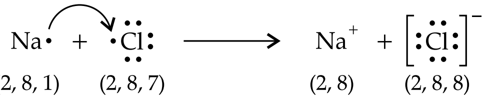
TIPS and TRICKS…

- *Learn and understand the chemical bond, its nature and types*
- *Understand the basic knowledge of octet rule*
- *Learn how a molecule is formed by various atoms?*
- *Learn properties of ionic and covalent compounds*

- In some molecules, the central atom cannot possibly have eight valence electrons. For example, LiCl, $BeCl_2$ and BCl_3 do not obey the octet rule.

❖ **Ionic or Electrovalent Bond :** "Ionic bonding is a type of chemical bond that involves the electrostatic attraction between oppositely charged ions together is known as ionic bond and electrovalent bond."

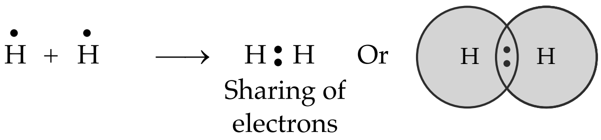
"Electrovalent compounds are those compounds in which constituent particles are ions or positively charged species and they are formed by transfer of electron from a metal to a non-metal.



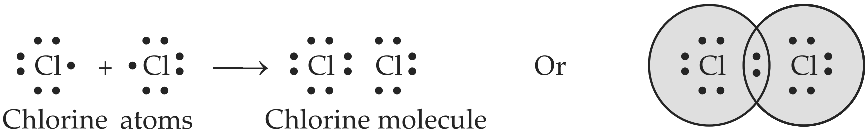
❖ **Properties of Ionic Compounds :**

- Ionic compounds have high melting points and high boiling points.
- They have higher enthalpies of fusion and vaporization than molecular compounds.
- They are hard and brittle.
- These compounds conduct electricity when they are dissolved in water or in molten state.
- Ionic solids are good insulators.
- The ionic bond is non-directional. This is because each ion is surrounded by oppositely charged ions uniformly distributed all around the ion.

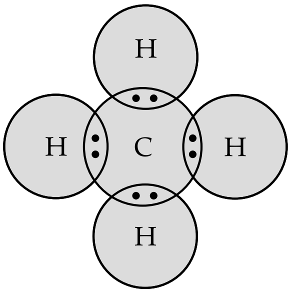
❖ **Covalent Bond :** A covalent bond is a chemical bond that involves the sharing of electron pairs between atoms. The stable balance of attractive and repulsive forces between atoms when they share electrons is known as covalent bonding.



Similarly, two chlorine atoms combine with each other to form a molecule of chlorine.



Methane (CH_4) :



Depending upon the number of 2, 4 or 6 electrons shared between two atoms, a covalent bond is called single, double or triple bond respectively.

❖ **Lewis Structure of Ionic Compounds**

(i) $(Na^+)\,(:\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}:^-)$ **(ii)** $(K^+)\,(:\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}:^-)$ **(iii)** $(Mg^{2+})\,(:\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}:^-)$

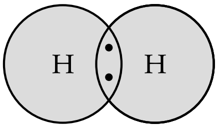
(iv) $(K^+)\,(:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:^{2-})$ **(v)** $(Mg^{2+})\,(:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:^{2-})$ **(vi)** $(Ca^{2+})\,(:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:^{2-})$

(vii) $(Na^+)\,(:\overset{\cdot\cdot}{\underset{\cdot\cdot}{S}}:^{2-})$ **(viii)** $(Na^+)\,(:\overset{\cdot\cdot}{\underset{\cdot\cdot}{P}}:^{3-})$ **(ix)** $(Li^+)\,(:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:^{2-})$

(x) $(Ca^{2+})\,(:\overset{\cdot\cdot}{\underset{\cdot\cdot}{N}}:^{3-})_2$

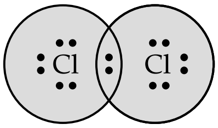
❖ **Lewis Structure of Covalent Compounds**

(i)



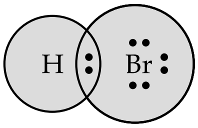
H—H

(ii)



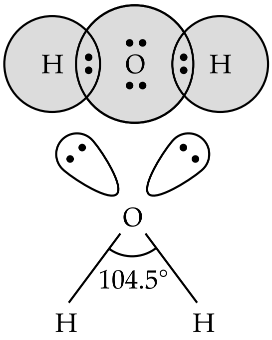
Cl—Cl

(iii)



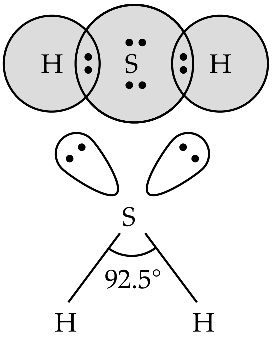
H—Br

(iv)



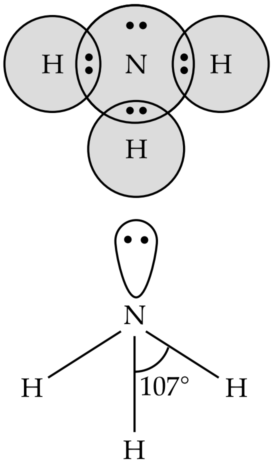
Bent molecule

(v)



Bent molecule

(vi)



Pyramidal

❖ **Formal Charge :** The formal charge of an atom in a polyatomic ion or molecule is defined as the difference between the number of valence electrons in an isolated atom and the number of electrons assigned to that atom in a Lewis structure.

It may be expressed as :

Formal charge on an atom in a Lewis structure =

(Total number of valence electrons in free atom) – (Total number of non-bonding (lone pair) electrons)

$$-\frac{1}{2}\text{(Total number of bonding (shared) electrons)}$$

$$FC = V - L - \frac{1}{2}S$$

where FC = Formal charge on an atom

V = Total number of valence electrons in the free atom

L = Total number of electrons present as non-bonding (lone pair)

S = Total number of bonding (shared) electrons.

❖ **Properties of Covalent Compounds**

- **Low melting and boiling points :** Covalent compounds consist of molecules held by weak forces. These can be easily overcome by heat.
- **Non-conductive nature :** Covalent compounds do not conduct electricity, i.e., electricity. This is because the covalent compounds do not contain ions or free electrons.
- **Solubility :** Covalent compounds are non-polar and do not dissolve in polar solvents like water. The covalent compounds, however, dissolve in non-polar solvents like benzene, toluene etc.
- **Slow rate of reaction :** The reaction of the covalent compounds are quite slow. The reaction is molecular and the molecular reactions are slow.
- **Bond order :** In the Lewis description of covalent bond, the bond order is given by the number of bonds between the two atoms in a molecule. Bond order in H_2 is one, in O_2, it is two and in N_2, it is three.

Isoelectronic molecules and ions have identical bond orders. For example, F_2 and O_2^{2-} have bond order 1 and N_2, CO and NO^+ have bond order 3.

The stabilities of molecules can be understood by the statement "**with increase in bond order, bond enthalpy increases and bond length decreases.**"

- **Types of Covalent Bond :** Depending upon the nature of combining atoms, the covalent bonds can be of two types :
  - **Non-polar Covalent Bond :** This type of bond is formed between the two atoms of the same element. Atoms of the same element attract electron equally. So, in other words, the shared electron pair will lie exactly midway between the two atoms. This type of covalent bond is described as a non-polar covalent bond.
    For example : H_2, O_2 and Cl_2 etc.
  - **Polar Covalent Bond :** This type of bond is formed between two atoms of different elements. The shared pair of electrons does not lie exactly midway between the two atoms. In fact, it lies more towards the atom which is more electronegative. The atom with higher affinity for electrons develops a slight negative charge and atom with lesser affinity for electrons develops a slight positive charge. For example, HCl, H_2O etc.
- **Dipole Moment :** It is defined as "the product of the magnitude of the charge and the distance of separation between the charges."

$$\text{Dipole moment } (\mu) = \text{Charge } (q) \times \text{Distance of separation } (d)$$

It is usually expressed in Debye (D).

Dipole moment is also expressed in the units of C m :

$$1\text{D} = 3.33564 \times 10^{-30} \text{ C m}$$

The dipole of HCl may be represented as :

$$\mathrm{H} \rightleftarrows \mathrm{Cl}$$

- **Valence Electrons :** The outermost shell electrons which take part in the formation of chemical bond are called valence electrons.
- **Lewis Symbols :** G.N. Lewis introduced simple notations to represent valence electrons in an atom, which are called Lewis symbols, e.g. ,
- **Octet Rule :** The rule by which atoms can combine either by transfer of valence electrons from one atom to another (gaining or losing) or by sharing of valence electrons in order to complete an octet in their valence shell is called octet rule.
- **Ionic Bond or Electrovalent Bond :** The bond formed, as a result of the electrostatic attraction between the positive and negative ions was termed as the ionic bond or electrovalent bond.
- **Covalent Bond :** The bond formed as a result of sharing of electron pairs between atoms is called covalent bond.
- **Single Covalent Bond :** When two atoms share one electron pair, they are said to be joined by a single covalent bond.
- **Double Bond :** If two atoms share two pairs of electrons, the covalent bond between them is called a double bond.
- **Triple Bond :** If two atoms share three pairs of electrons, the covalent bond between them is called a triple bond.
- **Lattice Enthalpy :** The lattice enthalpy of an ionic solid is defined as the energy required to completely separate one mole of a solid ionic compound into gaseous constituent ions.
- **Bond Length :** It 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.
- **Electrovalency :** The valence of an ion, equal to the number of positive or negative charges acquired by an atom through a loss or gain of electrons is known as electrovalency.
- **Polarizability :** The power of an ion to distort the other ion is polarizing power and the tendency of an ion to get distorted is called polarizability.
- **Covalency :** The bond formed between two atoms by mutual sharing of electrons between them so as to complete their octets is known as covalent bond and number of electrons involved is covalency.
- Under normal conditions, no other element exists as an independent atom in nature, except noble gases.
- Lewis postulated that atoms achieve the stable octet when they are linked by chemical bonds.
- In the periodic table, the highly electronegative halogens and the highly electropositive alkali metals are separated by the noble gases.

- ❖ The formation of a negative ion from a halogen atom and a positive ion from an alkali metal atom is associated with the gain and loss of an electron by the respective atoms.
- ❖ The negative and positive ions are stabilized by electrostatic attraction.
- ❖ The Lewis dot structures provide a picture of bonding in molecules and ions in terms of the shared pair of electrons and the octet rule.
- ❖ Generally the lowest energy structure is the one with the smallest formal charges on the atoms.
- ❖ The formal charge is a factor based on a pure covalent view of bonding in which electron pairs are shared equally by neighbouring atoms.

Multiple Choice Questions (1 mark each)

Q. 1. Polarity in a molecule and hence the dipole moment depends primarily on electronegativity of the constituent atoms and shape of a molecule. Which of the following has the highest dipole moment?

(i) CO_2 **(ii)** HI
(iii) H_2O **(iv)** SO_2

[NCERT Exemplar, Q. 2, Page 39]

Ans. Correct option : (iii)

Explanation : Being symmetrical, CO_2 has zero dipole moment. HI has dipole moment of 0.38 D while SO_2 has the same of 1.62 D. H_2O due to presence of maximum difference in electronegativity has dipole moment of 1.84 D.

Q. 2. In PO_4^{3-} ion the formal charge on the oxygen atom of P – O bond is

(i) + 1 **(ii)** – 1
(iii) –0.75 **(iv)** + 0.75

[NCERT Exemplar, Q. 5, Page 40]

Ans. Correct option : (ii)

Explanation : In PO_4^{3-} ion,the formal charge on the O atom of P – O bond =

(Number of valence electrons in free atom) – (Number of lone pair electrons + 1/2 Number of bonding electrons) = 6 – (6+ 1/2 × 2) =6 – 7 = –1

Q. 3. If the electronic configuration of an element is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2$, the four electrons involved in chemical bond formation will be –

(i) $3p^6$ **(ii)** $3p^6, 4s^2$
(iii) $3p^6, 3d^2$ **(iv)** $3d^2, 4s^2$

[NCERT Exemplar, Q. 12, Page 41]

Ans. Correct option : (iv)

Explanation : In transition elements, electrons of ns and (n – 1)d subshell take part in bond formation.

The electronic configurations of three elements, A, B and C are given below. Answer the questions 4 to 7 on the basis of these configurations

A $1s^2\ 2s^2\ 2p^6$
B $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$
C $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$

Q. 4. Stable form of A may be represented by the formula:

(i) A **(ii)** A_2
(iii) A_3 **(iv)** A_4

[NCERT Exemplar, Q. 14, Page 41]

Ans. Correct option : (i)

Explanation : The given electronic configuration is of a noble gas with a complete octet.

Q. 5. Stable form of C may be represented by the formula:

(i) C **(ii)** C_2
(iii) C_3 **(iv)** C_4

[NCERT Exemplar, Q. 15, Page 41]

Ans. Correct option : (ii)

Explanation : The given electronic configuration is of chlorine whose stable form is dichlorine.

Q. 6. The molecular formula of the compound formed by B and C will be

(i) BC **(ii)** B_2C
(iii) BC_2 **(iv)** BC_3

[NCERT Exemplar, Q. 16, Page 42]

Ans. Correct option : (iv)

Explanation : The given electronic configuration shows that B is phosphorus and C is chlorine. So the compound formed will be BC_3.

Q. 7. The bond between B and C will be

(i) Ionic **(ii)** Covalent
(iii) Hydrogen **(iv)** Coordinate

[NCERT Exemplar, Q. 17, Page 42]

Ans. Correct option : (ii)

Explanation : As both B and C are non-metals, the bond formed between them will be covalent in nature.

Q. 8. The electronic configuration of the outer most shell of the most electronegative element is

(i) $2s^22p^5$ **(ii)** $3s^23p^5$
(iii) $4s^24p^5$ **(iv)** $5s^25p^5$

[NCERT Exemplar, Q. 21, Page 42]

Ans. Correct option : (i)

Explanation : Electronic configuration in (i) is of fluorine while (ii), (iii) and (iv) are of chlorine, bromine and iodine respectively.

Q. 9. Amongst the following elements whose electronic configurations are given below, the one having the highest ionization enthalpy is

(i) $[Ne]3s^23p^1$ **(ii)** $[Ne]3s^23p^3$
(iii) $[Ne]3s^23p^2$ **(iv)** $[Ar]3d^{10}4s^24p^3$

[NCERT Exemplar, Q. 22, Page 43]

Ans. Correct option : (ii)

Explanation : Electronic configuration of (ii) and (iv) have half-filled p-orbital but (ii) being smaller in size will have highest ionization enthalpy.

Q. 10. Which of the following attain the linear structure:

(i) $BeCl_2$ **(ii)** NCO^+
(iii) NO_2 **(iv)** CS_2

[NCERT Exemplar, Q. 24, Page 43]

Ans. **Correct option :** (i) and (iv)

Explanation : NCO^+ is non-linear while NO_2 is angular.

Q. 11. CO is isoelectronic with

(i) NO^+ **(ii)** N_2

(iii) $SnCl_2$ **(iv)** NO_2^-

[NCERT Exemplar, Q. 25, Page 43]

Ans. **Correct option :** (i) and (ii)

Explanation : Number of electrons in CO = 14

Number of electrons in NO^+ = 14

Number of electrons in N_2 = 14

Number of electrons in $SnCl_2$ = 84

Number of electrons in NO_2^- = 24

Q. 12. Which of the following species have the same shape?

(i) CO_2 **(ii)** CCl_4

(iii) O_3 **(iv)** NO_2^-

[NCERT Exemplar, Q. 26, Page 43]

Ans. **Correct option :** (iii) and (iv)

Explanation : CO_2 – linear, CCl_4 – tetrahedral, O_3 - angular, NO_2^- – angular.

Assertion and Reason **(1 mark each)**

In the following questions a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the choices given below each question.

Q. 1. Assertion (A): Sodium chloride formed by the action of chlorine gas on sodium metal is a stable compound.

Reason : This is because sodium and chloride ions acquire octet in sodium chloride formation.

(i) A and R both are correct, and R is the correct explanation of A.

(ii) A and R both are correct, but R is not the correct explanation of A.

(iii) A is true but R is false.

(iv) A and R both are false

[NCERT Exemplar, Q. 57, Page 47]

Ans. **Correct option :** (i)

Q. 2. Assertion (A): Among the two O–H bonds in H_2O molecule, the energy required to break the first O–H bond and the other O–H bond is the same.

Reason : This is because the electronic environment around oxygen is the same even after breakage of one O–H bond.

(i) A and R both are correct, and R is the correct explanation of A.

(ii) A and R both are correct, but R is not the correct explanation of A.

(iii) A is true but R is false.

(iv) A and R both are false.

[NCERT Exemplar, Q. 59, Page 48]

Ans. **Correct option :** (iv)

Explanation : In case of H_2O molecule, the enthalpy needed to break the two O – H bonds is not the same. The difference in the Δ_aH^0 value shows that the second O–H bond energy undergoes some change because of changed chemical environment.

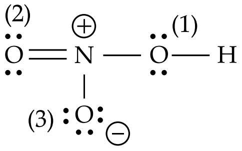
Short Answer Type Questions **(3 marks each)**

Q. 1. Write Lewis structure of the following compounds and show formal charge on each atom:

HNO_3, NO_2, H_2SO_4

[NCERT Exemplar, Q. 38, Page 45]

Ans. HNO_3 :



Formal charge on an atom

= [Total number of valence electrons in free atom]

– [total number of lone pairs of electrons]

$-\frac{1}{2}$ [total number of bonding electrons]

Formal charge on H $= 1-0-\frac{1}{2}\times 2 = 0$

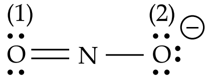
Formal charge on N $= 5-0-\frac{1}{2}\times 8 = +1$

Formal charge on O (1) $= 6-4-\frac{1}{2}\times 4 = 0$

Formal charge on O (2) $= 6-4-\frac{1}{2}\times 4 = 0$

Formal charge on O (3) $= 6-6-\frac{1}{2}\times 2 = -1$

NO_2 :

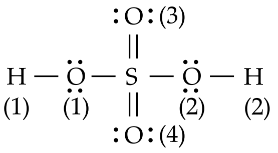


Formal charge on N $= 5-1-\frac{1}{2}\times 6 = +1$

Formal charge on O(1) $= 6-4-\frac{1}{2}\times 4 = 0$

Formal charge on O(2) $= 6-6-\frac{1}{2}\times 2 = -1$

H_2SO_4 :



$$\text{Formal charge on S} = 6 - 0 - \frac{1}{2} \times 12 = 0$$

$$\text{Formal charge on H(1)} = 1 - 0 - \frac{1}{2} \times 2 = 0$$

$$\text{Formal charge on H(2)} = 1 - 0 - \frac{1}{2} \times 2 = 0$$

$$\text{Formal charge on O(1)} = 6 - 4 - \frac{1}{2} \times 4 = 0$$

$$\text{Formal charge on O(2)} = 6 - 4 - \frac{1}{2} \times 4 = 0$$

$$\text{Formal charge on O(3)} = 6 - 4 - \frac{1}{2} \times 4 = 0$$

$$\text{Formal charge on O(4)} = 6 - 4 - \frac{1}{2} \times 4 = 0$$

Q. 2. Given reason for the following :

(i) Covalent bonds are directional bonds while ionic bonds are non-directional.

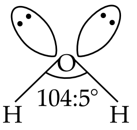
(ii) Water molecule has bent structure where as carbon dioxide molecule is linear.

(iii) Ethyne molecule is linear.

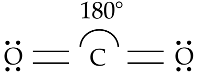
[NCERT Exemplar, Q. 41, Page 45]

Ans. (i) Covalent bonds are directional bonds because these bonds are formed by the overlapping of atomic orbitals while ionic bonds are non-directional because these bonds are formed by the transference of electrons and electrostatic field of an ion is present which is non-directional.

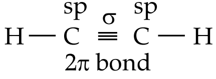
(ii) In H_2O, Oxygen atom is sp^3 hybridised. It contains two bond pairs and two lone pairs of electrons. The four sp^3 hybrid orbitals give distorted tetrahedral geometry due to lp – lp repulsion. The actual geometry is V-shape or bent structure with bond angle 104.5°.



In CO_2 molecule, carbon atom is sp hybridised. It contains two bond pairs and no lone pair of electrons. The two *sp* hybrid orbitals are oriented in opposite direction forming linear shape with bond angle 180°.



(iii) Ethyne molecule possesses sp hybridisation. Both the carbon atoms are sp hybridised. The two sp hybrid orbitals of both the carbon atoms are oriented in opposite direction forming the linear shape with bond angle 180°.



$$\underset{2\pi\ \text{bond}}{H - \overset{sp}{C} \overset{\sigma}{\equiv} \overset{sp}{C} - H}$$

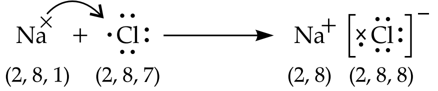
So, ethyne molecule is linear.

Q. 3. What is an ionic bond? With two suitable examples explain the difference between an ionic and a covalent bond?

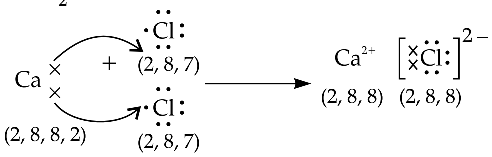
[NCERT Exemplar, Q. 42, Page 46]

Ans. Ionic bond: It is defined as the bond which is obtained by transference of electrons from one atom to other atom.

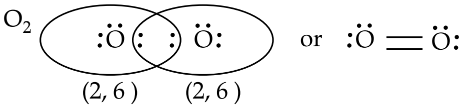
e.g. **NaCl**

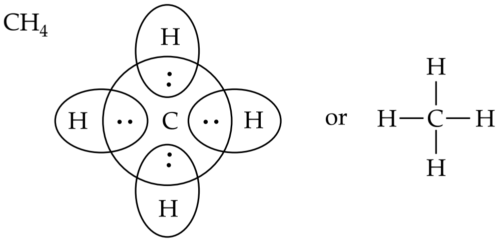


$CaCl_2$



Covalent bond: It is defined as the bonds which is formed be mutual sharing of electrons between them.





Q. 4. Arrange the following bonds in order of increasing ionic character giving reason.

N—H, F—H, C—H and O—H

[NCERT Exemplar, Q. 43, Page 46]

Ans. Ionic character of the bond depends on the difference of electronegativity. Greater the electronegativity difference between the two bonded atoms, greater is the ionic character.

Increasing order of electronegativity

$C < N < O < F$

Hence, increasing order of ionic character—

$C–H < N–H < O–H < F–H$

Q. 5. What is meant by the term average bond enthalpy? Why is there difference in bond enthalpy of O—H bond in ethanol (C_2H_5OH) and water?

[NCERT Exemplar, Q. 51, Page 46]

Ans. Average bond enthalpy : It is obtained by dividing total bond dissociation enthalpy by the number of bonds broken in polyatomic molecules.

In case of H_2O molecule, the enthalpy needed to break the two O—H bonds is not the same.

$$H_2O_{(g)} \longrightarrow H_{(g)} + OH_{(g)};\ \Delta_aH_1^{\ominus} = 502\ \text{kJ mol}^{-1}$$

$$OH_{(g)} \longrightarrow H_{(g)} + O_{(g)},\ \Delta aH_2^{\ominus} = 427\ \text{kJ mol}^{-1}$$

$$\text{Average bond enthalpy} = \frac{502 + 427}{2}$$

$$= 464.5\ \text{kJ mol}^{-1}$$

The difference in the $\Delta_aH^{\ominus}$ value shows that the second O–H bond undergoes some change because of changed chemical environment. This is the reason for some difference in energy of the same O–H bond in different molecules like C_2H_5OH (ethanol) and water.

Long Answer Type Questions

(5 marks each)

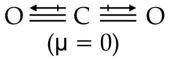
Q. 1. (i) Discuss the significance/applications of dipole moment.

(ii) Represent diagrammatically the bond moments and the resultant dipole moment in CO_2, NF_3 and $CHCl_3$.

[NCERT Exemplar, Q. 60, Page 48]

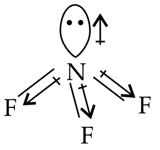
Ans. (i) For Answer, refer Q. 7 of short Answer Type Question

(ii) CO_2:



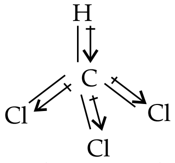
(μ = 0)

NF_3:



(μ = 0.24 D)

$CHCl_3$:



(μ = 1.03 D)

TOPIC-2

Resonance and VSEPR Theory

Quick Review

- ❖ **Resonance :** When a molecule cannot be represented by a single structure but its characteristic properties can be described by two or more than two structures, then actual structure is said to be a resonance hybrid of these structure.

TIPS and TRICKS...

Learn resonance and understand resonating structures

Understand VSEPR theory and its postulates

- ❖ **Conditions for Writing Resonating Structures** The essential conditions for writing resonating structures are given as below :
  - The contributing structures should have same atomic positions.
  - These structures should have same number of unpaired electrons.
  - These structures should have nearly same energy.
  - The structures should be so written that negative charge is present on an electronegative atom and positive charge is present on an electropositive atom.
  - In these structures, the like charges should not reside on adjacent atoms.
- ❖ Resonance stabilizes the molecule because the energy of the resonance hybrid is less than the energy of any single canonical structures.
- ❖ **Resonance Energy :** It is the difference between the actual bond energy of the molecule and that of the most stable resonating structures (having least energy). Thus,

Resonance energy = Actual bond energy – Energy of the most stable resonating structure

- ❖ **Valence Shell Electron Pair Repulsion (VSEPR) Theory :** In 1940, Sidgwick and Powell proposed a simple theory based on the repulsive interactions of the electron pairs in the valence shell of the atoms. It was further developed and refined by Nyholm and Gillespie in 1957.

  They suggested that the shapes of molecules can be determined by the number of electron pairs (bonding as well as non-bonding) in the valence shell of the central atom.

  This suggestion is the basis of valence shell electron pair repulsion (VSEPR) theory.

The basic idea of this theory is that bonded atoms in a molecule adopt that particular arrangement in space around the central atom which keeps them on the average as apart as possible.

❖ **Postulates of VSEPR Theory**

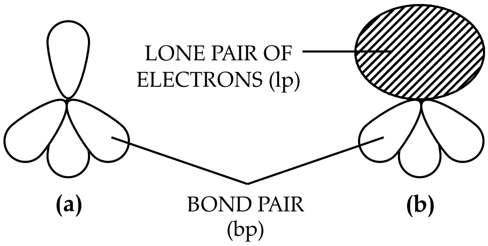
- The geometry of a molecule depends upon the total number of valence shell electron pairs (bonded or non-bonded) around the central atom in the molecule.
- Repulsion between valence shell electron pairs determines molecular shape. In order to minimize electron-electron repulsion or to acquire a state of minimum energy or maximum stability, the valence shell electron pairs keep themselves as far apart as possible.
- In case more than one geometrical arrangements are possible for a given number of bonded and non-bonded pairs, then the most stable arrangements are consistent with the following hypothesis :

(a) Repulsion between a lone pair and lone pair of electrons is different from that between the bond pairs or one lone pair and one bond pair. The repulsive interactions decrease in the order : Lone pair-Lone pair > Lone pair-Bond pair > Bond pair-Bond pair.

The presence of lone pairs in addition to bond pairs will result in certain distortions in the regular geometry of molecules.

(b) Repulsive forces decrease sharply with increasing angle between the electron pairs. They are strong at 90°, much weaker at 120° and very weak at 180°.

Thus, the molecules in which the central atom is surrounded only by similar bonded electron pairs will have regular geometries while those in which the central atom is surrounded by bond pairs as well as lone pairs will have irregular geometries.



Effect of lone pair of electrons (a) Four orbitals having bond pair electrons (b) three orbitals with bond pair electron and one orbital with lone pair electrons (angle between orbitals with bond pair electrons decreases)

❖ **Resonance :** The delocalization of a pair of electrons in a molecule or ion which results in observed bond length, bond order, bond energy different from normal covalent bond is called resonance.

❖ **Resonance Hybrid :** The structure which is near to all resonating structures and nearly explain the property of that molecule or ion is called resonance hybrid.

❖ The shape of a molecule depends upon the number of valence shell electron pairs (bonded or non-bonded) around the central atom.

❖ The repulsive interaction of electron pairs decrease in the order –

lp – lp > lp – bp > bp – bp

(where, lp = lone pair, bp = bond pair)

Multiple Choice Questions **(1 mark each)**

Q. 1. In NO_3^- ion, the number of bond pairs and lone pairs of electrons on nitrogen atom are

(i) 2, 2 **(ii)** 3, 1

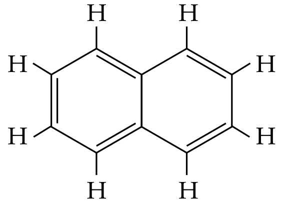
(iii) 1, 3 **(iv)** 4, 0

[NCERT Exemplar, Q. 6, Page 40]

Ans. Correct option : (iv)

Explanation : Nitrogen atom contains five valence electrons. As −ve charge is present, number of valence electrons is 5 + 1 = 6. One O-atom forms double bond and two O-atoms shared with two electrons of N-atoms. So, 3 O-atoms shared with 8 electrons of N-atoms. Hence No. of bond pairs = 4, No. of lone pairs = 0

Q. 2. Number of π bonds and σ bonds in the following structure is –



(i) 6, 19 **(ii)** 4, 20

(iii) 5, 19 **(iv)** 5, 20

[NCERT Exemplar, Q. 8, Page 40]

Ans. Correct option : (iii)

Explanation : No. of C=C bonds (pi bonds) = 5

No. of C-H (sigma bonds) = 8 and No. of C-C (sigma bonds) = 11

Total sigma bonds = 19

Q. 3. Which of the following statements are not correct?

(i) NaCl being an ionic compound is a good conductor of electricity in the solid state.

(ii) In canonical structures there is a difference in the arrangement of atoms.

(iii) Hybrid orbitals form stronger bonds than pure orbitals.

(iv) VSEPR Theory can explain the square planar geometry of XeF_4.

[NCERT Exemplar, Q. 30, Page 44]

Ans. Correct option : (i) and (ii)

Explanation : (i) Ionic compounds are good conductors of electricity only in molten state.

(ii) In canonical structures there is a difference in the arrangement of electrons.

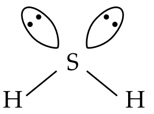
Short Answer Type Questions

(3 marks each)

Q. 1. Explain the non-linear shape of H_2O and non-planar shape of PCl_3 using valence shell electron pair repulsion theory.

[NCERT Exemplar, Q. 31, Page 44]

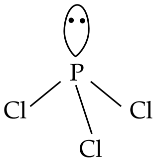
Ans. H_2S : In H_2S, the central atom S contains 6 valence electrons ($_{16}S$ = 2, 8, 6). Out of which, two electrons are used to form bonds with two hydrogen atoms and the remaining four electrons are present as two lone pairs



Due to presence of two lone pairs in H_2S, the shape of H_2S becomes distorted tetrahedral or angular or bent i.e. non-linear.

PCl_3 : $_{15}P$ = 2, 8, 5

In PCl_3, the central atom phosphorus contains 5 valence electrons. Out of which, three electrons are used to make bonds with three Cl-atoms. The remaining two electrons are present as one lone pair.

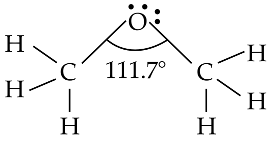


Due to presence of one lone pair in PCl_3, the shape of PCl_3 becomes pyramidal i.e. non-planar.

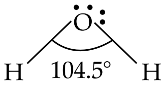
Q. 2. In both water and dimethyl ether ($CH_3 - \ddot{\underset{\cdot\cdot}{O}} - CH_3$), oxygen atom is central atom, and has the same hybridisation, yet they have different bond angles. Which one has greater bond angle? Give reason. [NCERT Exemplar, Q. 37, Page 45]

Ans. Dimethyl ether will have greater bond angle than water. It is due to more repulsion between bond pair of – CH_3 groups attached in dimethyl ether as compared to bond pairs of H-atoms attached in water.

Actually carbon atom of $-CH_3$ group is attached to three H-atoms through σ-bonds. These three C-H bond pair of electrons increases the electronic charge density on carbon atom, due to which, repulsion between two $-CH_3$ groups will be more than that between two H-atoms.



Dimethyl ether

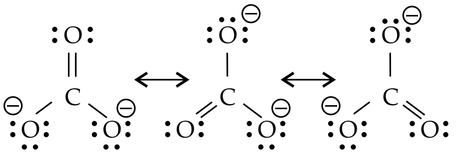


Water

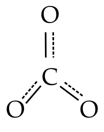
Q. 3. Explain why CO_3^{2-} ion cannot be represented by a single Lewis structure. How can it be best represented?

[NCERT Exemplar, Q. 44, Page 46]

Ans. CO_3^{2-} ion can not be represented by a single Lewis structure because a single Lewis structure can not explain all the properties of this ion. It can be best represented as a resonance hybrid of the following resonating structures:



Resonating Structures



Resonance hybrid

Q. 4. Group the following as linear and non-linear molecules :

H_2O, HOCl, $BeCl_2$, Cl_2O

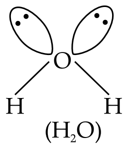
[NCERT Exemplar, Q. 46, Page 46]

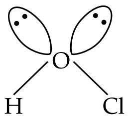
Ans. Linear molecule :

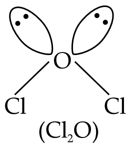
Cl —Be—Cl

($BeCl_2$)

Non linear molecule :


(H_2O)

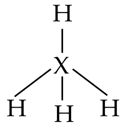

(HOCl)


(Cl_2O)

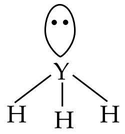
Q. 5. Elements X, Y and Z have 4, 5 and 7 valence electrons respectively. (i) Write the molecular formula of the compounds formed by these elements individually with hydrogen. (ii) Which of these compounds will have the highest dipole moment?

[NCERT Exemplar, Q. 47, Page 46]

Ans. (i) XH_4 (when element x contains 4 valence electrons)



YH_3 (when element Y contains 5 valence electrons)



HZ (when element Z contains 7 valence electrons)

$H-\ddot{\underset{..}{Z}}:$

(ii) The element Z contains seven valence electrons. So, it is the most electronegative element. Hence the compound HZ will have the highest dipole moment.

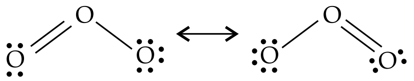
Q. 6. Draw the resonating structure of

(i) Ozone molecule

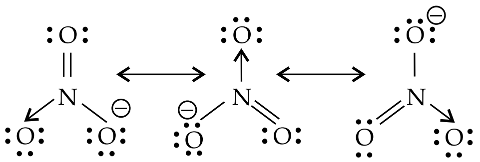
(ii) Nitrate ion

[NCERT Exemplar, Q. 48, Page 46]

Ans. **(i)** The resonating structures of ozone molecule are:



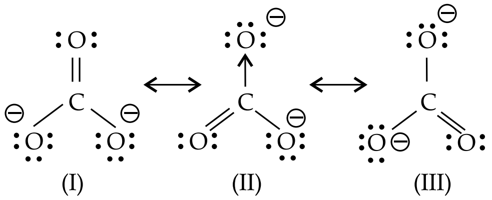
(ii) The resonating structures of nitrate ion are :



Q. 7. All the C—O bonds in carbonate ion (CO_3^{2-}) are equal in length. Explain.

[NCERT Exemplar, Q. 50, Page 46]

Ans. In CO_3^{2-} ion, carbon is bonded to three oxygen atoms. It is bonded to two oxygen atoms by double bonds and one with single bond. These bonds are not fixed and exhibit resonance. So, all C—O bonds in carbonate ion (CO_3^{2-}) are equal in length. The resonating structures of CO_3^{2-} are shown as below:



TOPIC-3

Valence Bond Theory, Hybridisation, Molecular Orbital Theory and Hydrogen Bonding

Quick Review

- According to V.B.T., a covalent bond is formed between the two atoms by the overlap of half filled valence atomic orbitals of each atom containing one unpaired electron.
- The bond is formed when two atoms approach each other in such a way that occupied orbitals with similar energies are able to overlap.
- Greater the overlap, stronger is the bond.

TIPS and TRICKS...

- *Understand VBT and MOT.*
- *Learn the concept of hybridization.*
- *How molecular orbitals are formed in a diatomic molecule or ion?*
- *Understand hydrogen bonding, its types and consequences.*

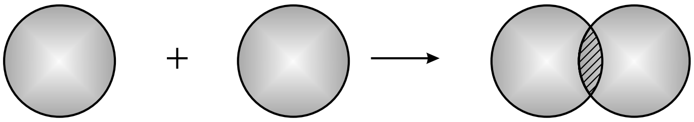
- **Types of Overlapping and Nature of Covalent Bonds**

  Depending upon the type of overlapping, the covalent bonds may be divided into two types :

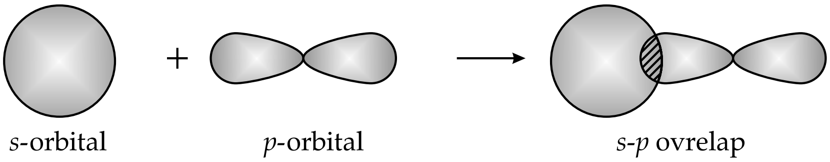
  (a) Sigma (σ) bond and **(b)** Pi (π) bond

  (a) Sigma (σ) bond : This type of covalent bond is formed by the end to end (head on) overlapping of bonding orbitals along the internuclear axis. The overlap is known as **head on** or **axial** overlap. The sigma bond is formed by any one of the following types of combinations of atomic orbitals :

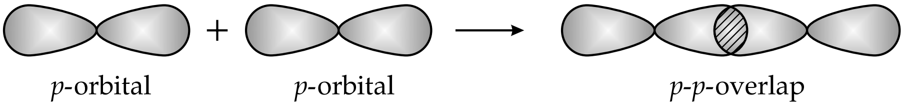
  (i) *s-s* overlapping : In this type, two half-filled *s*-orbitals overlap along the internuclear axis as shown below.



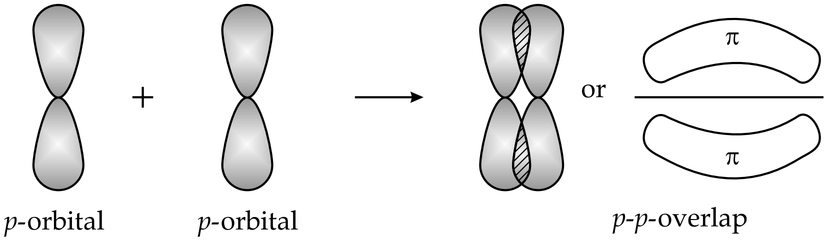
  (ii) *s-p* overlapping : This type of overlapping between the half-filled *s*-orbital of one atom and *p*-orbital of the other atom.



  (iii) *p-p* overlapping : This type of overlapping occurs between half-filled *p*-orbitals of the two approaching atoms.



  (b) Pi (π) bond : This type of covalent bond is formed by the sidewise overlap of the half-filled atomic orbitals of bonding atoms. Such an overlap is known as **sidewise** or **lateral overlap**. The atomic orbitals overlap in such a way that their axis remain parallel to each other and perpendicular to the internuclear axis. The orbital obtained as a result of sidewise overlap consists of two saucer type charged clouds above and below the plane of the participating atoms.



- **Strength of sigma and pi-bonds :** The strength of a covalent bond depends upon the extent of overlapping of atomic orbitals forming the bond. During the formation of a sigma bond, the overlapping of orbitals takes place to a larger extent.
- On the other hand, during the formation of a pi-bond, the overlapping occurs to a smaller extent. Therefore, a sigma bond is strong than a pi-bond.
- **Hybridisation :** According to Pauling, to account for the shapes of polyatomic molecules, the atomic orbitals combine to form new set of equivalent orbitals known as hybrid orbitals, are used in bond formation. This process is known as hybridisation. This may be defined as—

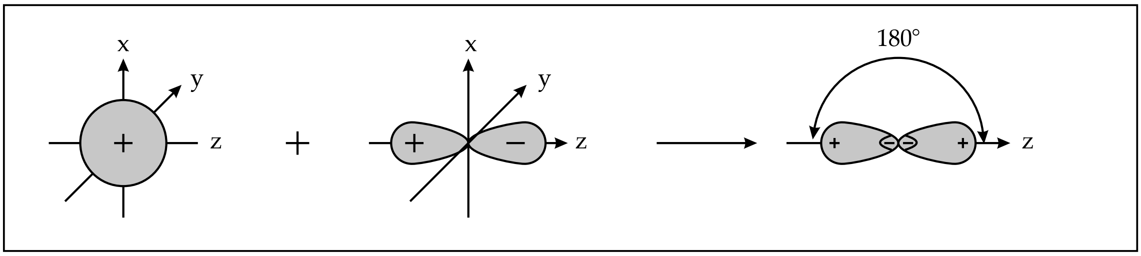
  "The process of intermixing of the orbitals of slightly different energies so as to redistribute their energies resulting in the formation of new set of orbitals of equivalent energies and shape."
- **Characteristics of Hybridisation**
  - The number of hybridised orbitals is equal to the number of the orbitals that get hybridised.
  - The hybridised orbitals are always equivalent in energy and shape.
  - The hybrid orbitals are more effective in forming stable bonds than the pure atomic orbitals.
  - The hybrid orbitals are directed in space in some preferred directions to have stable arrangement. Therefore, the type of hybridisation indicates the geometry of the molecule.
- **Conditions for Hybridisation**
  - Only the orbitals present in the valence shell of the atom are hybridised.
  - The orbitals undergoing hybridisation should have only a small difference in energy. The orbitals which differ largely in energy cannot take part in hybridisation.

- Promotion of electron is not essential condition prior to hybridisation.
- It is not essential that only half filled orbitals participate in hybridisation. In certain cases, even filled orbitals of valence shell participate in hybridisation.

There are many types of hybridisation involving different atomic orbitals. The different types of hybridisation are discussed below :

❖ Types of Hybridisation

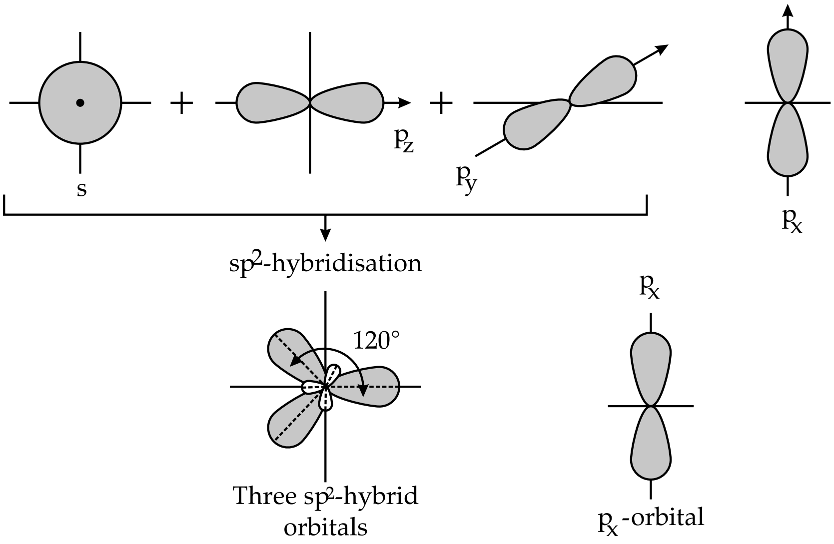
- ***sp* Hybridisation :** In *sp* hybridisation, one *s* and one *p* orbital mix and form two equivalent *sp* hybrid orbitals. The orbitals suitable for *sp* hybridisation are *s* and p_z orbitals, if the hybrid orbitals lie along Z-axis. Each *sp* hybrid orbital has 50% *s*-character and 50% *p*-character. These two *sp* hybrid orbitals are oriented in opposite direction forming an angle of 180°. The *sp*-hybridisation is pictorially shown as below :



Formation of *sp* hybrid orbitals

Example : BeF_2, $BeCl_2$ etc.

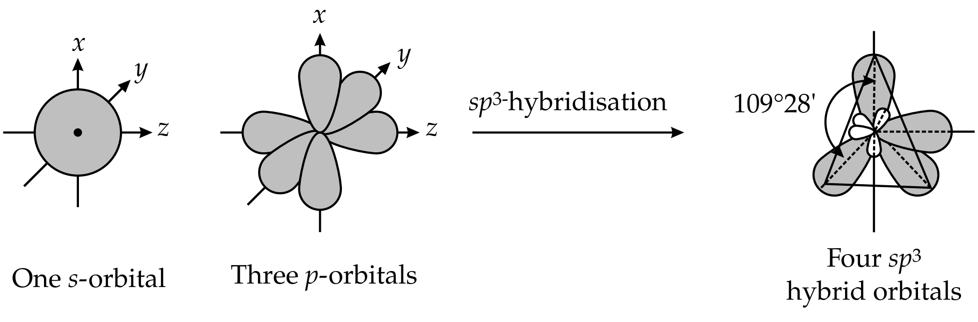
- ***sp*^{2} Hybridisation :** The combination of one *s* and two *p* orbitals gives rise to three *sp*^{2} hybrid orbitals. These three hybrid orbitals lie in the same plane and are directed towards the three corners of an equilateral triangle in a plane having an angle of 120°. Each *sp*^{2} hybrid orbital has 33·3% *s*-character and 66·7% *p*-character.



Formation of *sp*^{2} hybrid orbitals

Example : BCl_3, BF_3 etc.

- ***sp*^{3} Hybridisation :** In *sp*^{3} hybridisation, one *s* and three *p* orbitals mix and form four *sp*^{3} hybrid orbitals of equivalent energies and shape. Each *sp*^{3} hybrid orbitals has 25% s-character and 75% p-character. The four *sp*^{3} hybrid orbitals are directed towards the four corners of the tetrahedron. The angle between *sp*^{3} hybrid orbital is 109°28′.



Formation of *sp*^{3} hybrid orbitals

Example : CH_4, CCl_4 etc.

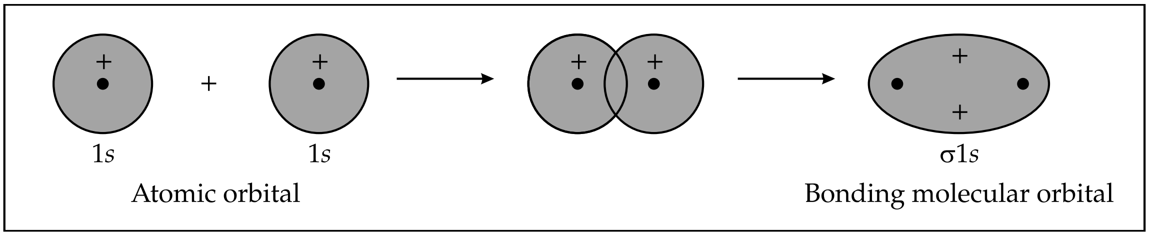
❖ Molecular Orbital Theory

Molecular orbital theory was proposed by F. Hund and R.S. Mulliken in 1932. The basic idea of molecular orbital theory is that atomic orbitals of individual atoms combine to form molecular orbitals.

The electrons in molecules are present in the molecular orbitals which are associated with several nuclei. These molecular orbitals are filled in the same way as the atomic orbitals in atoms are filled.

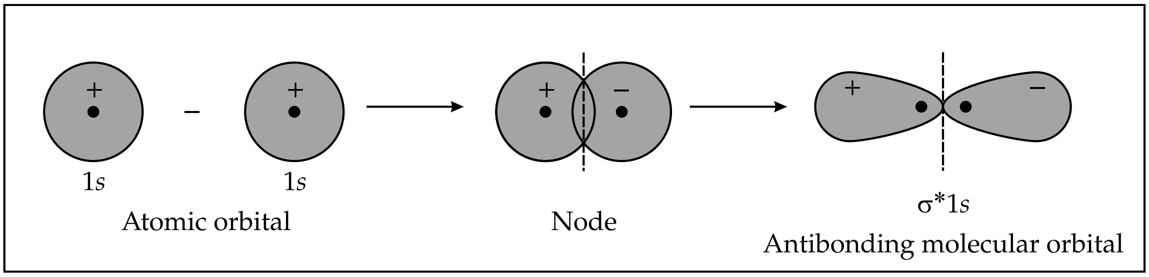
Salient Features of Molecular Orbital Theory

- Just like an atom, molecule has orbitals of definite energy levels. Like electrons of atoms are present in atomic orbitals, electrons of a molecule are present in different molecular orbitals.
- Molecular orbitals are formed by the combination of atomic orbitals of proper symmetry and comparable energies. The atomic orbitals of these atoms merge into molecular orbitals.
- An electron in an atomic orbital is under the influence of only one nucleus. However, an electron in a molecular orbital is under the influence of two or more nuclei depending upon the number of atoms present in the molecule.
- The number of molecular orbitals formed is equal to the number of combining atomic orbitals. When two atomic orbitals combine, they form two molecular orbitals. These are called bonding molecular orbital and anti-bonding molecular orbital.
- The bonding molecular orbital has lower energy and hence greater stability whereas corresponding anti-bonding molecular orbital has more energy and hence lesser stability.
- The molecular orbital formed by the addition of two atomic orbitals is called bonding molecular orbital. It is shown in following figure :



Formation of bonding molecular orbital

- The molecular orbital formed by the subtraction of two atomic orbitals is called anti-bonding molecular orbital. It is shown in following figure :



Formation of anti-bonding molecular orbital

It is clear from the figure that the electron density in between the two nuclei is practically zero and is concentrated in regions away from each nucleus. In this case, the electron probability densities of two atomic orbitals get cancelled in the centre (by subtraction) so that there is no probability of finding the electron in the region of overlap i.e. between the nuclei. This situation does not favour the bond formation. Such an orbital is called anti-bonding molecular orbital. It is designated as σ*1*s* (called sigma star 1*s*). The asterisk '*' is used to represent anti-bonding molecular orbital.

❖ **Conditions for the Combination of Atomic Orbitals :** Molecular orbitals are formed by the combination of atomic orbitals. But all types of orbitals cannot combine with each other. The following are the main conditions for effective combination of atomic orbitals.

- The combining atomic orbitals must have same or nearly the same energies.
- The extent of overlapping between the atomic orbitals of two atoms should be large.

❖ Types of Molecular Orbitals

- **Bonding molecular orbitals :** A molecular orbital that is obtained by the addition overlap (*i.e*, when the lobes of atomic orbital overlap with the same sign) of two atomic orbitals is known as bonding molecular orbital. The energy of bonding molecular orbital is less than that of the constituent overlapping atomic orbitals. The difference in energy between the combining atomic orbitals and the bonding molecular orbital formed, is called the stabilisation energy, because, it stabilizes the molecule.

- **Non-bonding molecular orbitals :** Orbitals, which are completely inside the closed shell of atom, do not play any part in the formation of molecule. They remain unaffected and are termed as non-bonding molecular orbitals. When atomic orbitals do not interact with each other, formation of non-bonding molecular orbitals takes place. The reasons for no interaction may be one of the following :
  (i) One orbital is far away from other orbital, so overlapping is not possible.
  (ii) Symmetries of atomic orbitals are not same.
  (iii) Energies of atomic orbitals are not same.
- **Anti-bonding molecular orbitals** : A molecular orbital that is obtained by the subtraction overlap (i.e., when the lobes of atomic orbitals overlap with the opposite sign) of two atomic orbitals is known as anti-bonding molecular orbital. The energy of anti-bonding molecular orbital is higher than that of the constituent overlapping atomic orbitals. The difference in energy between the anti-bonding molecular orbital and the combining atomic orbital is known as destabilisation energy, because it destabilizes the molecule.

  For molecules O_2 onwards, the increasing order of energies for molecular orbitals in which they are filled is as follows :

  $\sigma 1s, \sigma^* 1s, \sigma 2s, \sigma^* 2s, \sigma 2p_z, (\pi 2p_z = \pi 2p_y), (\pi^* 2p_z = \pi^* 2p_y), \sigma^* 2p_z$

❖ However, for homonuclear diatomic molecules of second row elements such as, Li_2, Be_2, B_2, C_2, N_2 the $\sigma 2p_z$ MO is higher in energy than $\pi 2p_x$ and $\pi 2p_y$ MOs.

The increasing order of energies for MOs for their molecules is

$\sigma 1s, \sigma^* 1s, \sigma 2s, \sigma^* 2s, (\pi 2p_x = \pi 2p_y), \sigma 2p_z, (\pi^* 2p_x = \pi^* 2p_y), \sigma^* 2p_z$

❖ The filling of molecular orbitals takes place by following the rules of Aufbau principle, Pauli's exclusion principle and Hund's rule in the similar way as for atomic orbitals.

❖ Presence of unpaired electron shows that molecule is paramagnetic, however, paired electrons show that it is diamagnetic.

❖ **Hydrogen Bonding :** When hydrogen atom is bonded to atoms of highly electronegative elements such as fluorine, oxygen or nitrogen, the hydrogen atom forms a weak bond with the electronegative atom of the other molecule. This weak bond is called hydrogen bond. For example, in hydrogen fluoride, HF, hydrogen atom forms a weak bond with fluorine atom of the high bonding molecule while remaining bonded to its fluorine atom. This may be shown as :

H—F .... H—F .... H—F ....

In other words, hydrogen atom acts as a bridge between two atoms, holding one atom by a covalent bond and the other atom by a hydrogen bond. The hydrogen bond is represented by dotted line (...........) while the covalent bond is represented by solid line (—).

❖ **Types of Hydrogen Bond:** Hydrogen bond can be classified into two types :

(a) Intermolecular hydrogen bond
(b) Intramolecular hydrogen bond

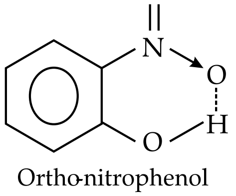
(a) Intermolecular hydrogen bond : Intermolecular hydrogen bond is formed between different molecules of the same or different substances.

For example,

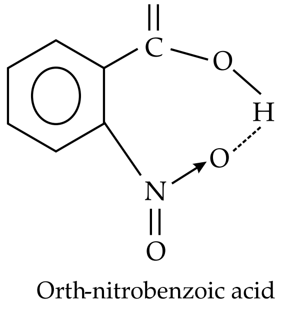
(i) hydrogen bond between the molecules of hydrogen fluoride.
(ii) hydrogen bond in alcohol or water molecules.

(b) Intramolecular hydrogen bond : Intramolecular hydrogen bond is formed between the hydrogen atom and the highly electronegative atom (F, O or N) present in the same molecule.

Intramolecular hydrogen bond results in the cyclisation of the molecule and prevents its association. Consequently, the effect of intramolecular hydrogen bond on the physical properties is negligible.



Ortho-nitrophenol



Orth-nitrobenzoic acid

- **Applications of Intermolecular H-bonding**
  - **Melting point and boiling point of water :** Water has the lowest molecular weight among the hydrides of group 16 elements yet it has the highest melting and boling points. It is due to intermolecular H–bonding in H_2O.
  - **Ice has less density than water :** In crystal structure of ice, every water molecule is associated with four other water molecules by H-bonding in a cage like tetrahedral structure. On melting, H-bonds in the ice are broken and space between water molecules decreases and density of water increases up to 4°C. Above 4°C, more H-bond are broken. The water molecules get apart from each other and the density again decreases. Thus, water has maximum density at 4°C.
- **Sigma (σ) bond :** The covalent bond which is formed by the end to end (head on) overlap of bonding orbitals along the internuclear axis is called sigma (σ) bond.
- **Pi (π) bond :** The covalent bond which is formed by the sidewise overlap of bonding orbitals perpendicular to the internuclear axis is called pi (π) bond.
- **Hybridisation :** It is defined as the process of intermixing of the orbitals of slightly different energies so as to redistribute their energies resulting in the formation of new set of orbitals of equivalent energies and shape.
- **Bonding Molecular Orbital :** The molecular orbital which is formed by addition of two atomic orbitals is called bonding molecular orbital.
- **Anti-bonding Molecular Orbital :** The molecular orbital which is formed by subtraction of two atomic orbitals is called anti-bonding molecular orbital.
- **Bond Order :** It is defined as one half the difference between the number of electrons present in the bonding and the anti bonding orbitals. [Bond order = $\frac{1}{2}(N_b - N_a)$]
- **Hydrogen Bond :** It can be defined as the attractive force which binds hydrogen atom of one molecule with the electronegative atom (F, O or N) of another or same molecule.
- The extent of overlap decides the strength of a covalent bond. Generally, greater the overlap, the stronger is the bond formed between two atoms.
- According to orbital overlap concept, the formation of a covalent bond between two atoms results by pairing of electrons present in the valence shell having opposite spins.
- When orbitals of two atoms come close to form bond, their overlap may be positive, negative or zero depending upon the sign (phase) and direction of orientation of amplitude of orbital wave function in space.
- According to concept of hybridization, the atomic orbitals combine to form new set of equivalent orbitals known as hybrid orbitals.
- The number of hybrid orbitals is equal to the number of the atomic orbitals that get hybridised.
- The hybridised orbitals are always equivalent in energy and shape.
- The orbitals present in the valence shell of the atom are hybridised.
- The orbitals undergoing hybridization should have almost equal energy.
- The sigma (σ) molecular orbitals are symmetrical around the bond axis whereas pi (π) molecular orbitals are not symmetrical.
- The increasing order of energies of various molecular orbitals in case of O_2 or F_2 :
  $\sigma1s < \sigma^*1s < \sigma2s < \sigma^*2s < \sigma2p_z < (\pi2p_x = \pi2p_y) < (\pi^*2p_x = \pi^*2p_y) < \sigma^*2p_z$
- The increasing order of energies of various molecular orbitals in case of Li_2, Be_2, B_2, C_2 or N_2 :
  $\sigma1s < \sigma^*1s < \sigma2s < \sigma^*2s < (\pi2p_x = \pi2p_y) < \sigma2p_z < (\pi^*2p_x = \pi^*2p_y) < \sigma^*2p_z$
- The distribution of electrons among various molecular orbitals is called the **electronic configuration** of the molecule.
- The bond length decreases as bond order increases.
- If all the molecular orbitals in a molecule are doubly occupied, the substance is said to be **diamagnetic** (repelled by magnetic field).
- If one or more molecular orbitals are singly occupied, the substance is said to be **paramagnetic** (attracted by magnetic field).

- The bond strength increases as bond order increases.
- The bond dissociation energy increases as bond order increases.
- Density of H_2O is maximum at 4° due to strongest intermolecular hydrogen bonding.
- Bond order zero means no possibility of that molecule.
- Bond order = $\frac{1}{2}(N_b - N_a)$

Where N_b = No. of electrons in bonding molecular orbital
N_a = No of electrons in anti-bonding molecular orbital.

Multiple Choice Questions

(1 mark each)

Q. 1. Isostructural species are those which have the same shape and hybridization. Among the given species identify the isostructural pairs.

(i) [NF_3 and BF_3] **(ii) [BF_4^- and NH_4^+]**
(iii) [BCl_3 and $BrCl_3$] **(iv) [NH_2 and NO_3^-]**

[NCERT Exemplar, Q. 1, Page 39]

Ans. Correct option : (ii)

Explanation : (i) NF_3 is pyramidal whereas BF_3 is triangular planar.
(ii) BF_4^- and NH_4^+ are tetrahedral.
(iii) BCl_3 is triangular planar whereas $BrCl_3$ is pyramidal.
(iv) NH_3 is pyramidal whereas NO_3 is triangular planar.

Q. 2. The types of hybrid orbitals of nitrogen in NO_2^+, NO_3^- and NH_4^+ respectively are expected to be

(i) *sp*, *sp*^{3} **and** *sp*^{2} **(ii)** *sp*, *sp*^{2}, **and** *sp*^{3}
(iii) *sp*^{2}, *sp and sp*^{3} **(iv)** *sp*^{2}, *sp*^{3} **and** *sp*

[NCERT Exemplar, Q. 3, Page 39]

Ans. Correct option : (ii)

Explanation : Number of orbitals involved in hybridization (H) = 1/2 [V+M-C+A]

where V= valence electrons of central atom
M = no. of monovalent atoms linked with central atom
C = charge of cation
A = charge of anion

NO_2^+ = 1/2 [5+0-1+0] = 2 or sp
NO_3^- = 1/2 [5+0-0+1] = 3 or sp^2
NH_4^+ = 1/2 [5+4-1+0] = 4 or sp^3

Q. 3. Hydrogen bonds are formed in many compounds e.g. H_2O, HF, NH_3. The boiling point of such compounds depends to a large extent on the strength of hydrogen bond and the number of hydrogen bonds. The correct decreasing order of the boiling points of above compounds is:

(i) HF > H_2O > NH_3
(ii) H_2O > HF > NH_3
(iii) NH_3 > HF > H_2O
(iv) NH_3 > H_2O > HF

[NCERT Exemplar, Q. 4, Page 39]

Ans. Correct option : (ii)

Explanation : Strength of hydrogen bonding:

HF > H_2O > NH_3

Also, each H_2O molecule is linked with four H_2O molecules through H-bonds while each HF molecule is linked only to two HF molecules. Therefore, the decreasing order of boiling points will be H_2O > HF > NH_3

Q. 4. Which of the following species has tetrahedral geometry?

(i) BH_4^- **(ii) NH_2^-**
(iii) CO_3^{2-} **(iv) H_3O^+**

[NCERT Exemplar, Q. 7, Page 40]

Ans. Correct option : (i)

Explanation : BH_4^- shows sp^3 hybridization.

Q. 5. Which molecule/ion out of the following does not contain unpaired electrons?

(i) N_2^+ **(ii) O_2**
(iii) O_2^{2-} **(iv) B_2**

[NCERT Exemplar, Q. 9, Page 40]

Ans. Correct option : (iii)

Explanation : O_2^{2-} has all paired electrons.

Q. 6. In which of the following molecule/ion all the bonds are not equal?

(i) XeF_4 **(ii) BF_4^-**
(iii) C_2H_4 **(iv) SiF_4**

[NCERT Exemplar, Q. 10, Page 41]

Ans. Correct option : (iii)

Explanation : XeF_4 : square planar, all bonds are equal.
BF_4^- : tetrahedral, all bonds are equal.
C_2H_4 : C = C bond is not equal to C – H bond.
SiF_4 = tetrahedral, all bonds are equal.

Q. 7. In which of the following substances will hydrogen bond be strongest?

(i) HCl **(ii) H_2O**
(iii) HI **(iv) H_2S**

[NCERT Exemplar, Q. 11, Page 41]

Ans. Correct option : (ii)

Explanation : Cl, I and S do not form H bonds as their difference in electronegativity with H is not large enough. Only H_2O forms hydrogen bond and one H_2O molecule is joined by four H_2O molecules.

Q. 8. Which of the following angle corresponds to sp^2 hybridisation?

(i) 90° **(ii)** 120°

(iii) 180° **(iv)** 109°

[NCERT Exemplar, Q. 13, Page 41]

Ans. Correct option : (ii)

Explanation : The bond angle in sp^2 hybridisation is 120°.

Q. 9. Which of the following order of energies of molecular orbitals of N_2 is correct?

(i) $(\pi 2p_y) < (\sigma 2p_z) < (\pi^* 2p_x) \approx (\pi^* 2p_y)$

(ii) $(\pi 2p_y) > (\sigma 2p_z) > (\pi^* 2p_x) \approx (\pi^* 2p_y)$

(iii) $(\pi 2p_y) < (\sigma 2p_z) > (\pi^* 2p_x) \approx (\pi^* 2p_y)$

(iv) $(\pi 2p_y) > (\sigma 2p_z) < (\pi^* 2p_x) \approx (\pi^* 2p_y)$

[NCERT Exemplar, Q. 18, Page 42]

Ans. Correct option : (i)

Q. 10. Which of the following statement is not correct from the view point of molecular orbital theory?

(i) **Be_2 is not a stable molecule.**

(ii) **He_2 is not stable but He_2^+ is expected to exist.**

(iii) **Bond strength of N_2 is maximum amongst the homonuclear diatomic molecules belonging to the second period.**

(iv) **The order of energies of molecular orbitals in N_2 molecule is**

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

[NCERT Exemplar, Q. 19, Page 42]

Ans. Correct option : (iv)

Explanation : (i) $Be_2 = \sigma 1s^2\, \sigma^* 1s^2\, \sigma 2s^2\, \sigma^* 2s^2$

$$\text{Bond order} = \frac{4-4}{2} = 0$$

So, being unstable it does not exist.

(ii) $He_2 = \sigma 1s^2\, \sigma^* 1s^2$

$$\text{Bond order} = \frac{2-2}{2} = 0$$

So, being unstable it does not exist.

$He_2^+ = \sigma 1s^2\, \sigma^* 1s^1$

$$\text{Bond order} = \frac{2-1}{2} = 0.5$$

So, being stable it is expected to exist.

(iii) $N_2 = \sigma 1s^2\, \sigma^* 1s^2\, \sigma 2s^2\, \sigma^* 2s^2\, \pi 2px^2 = \pi 2py^2\, \sigma 2pz^2$

$$\text{Bond order} = \frac{10-4}{2} = 3$$

Thus, dinitrogen molecule has triple bond while no molecule of second period has more than double bond. Thus, its bond strength is maximum amongst the homonuclear diatomic molecules belonging to second period.

(iv) The correct order of N_2 molecule is $\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < (\pi 2px^2 = \pi 2py) < \sigma 2pz < \pi^* 2px = \pi 2py < \sigma^* 2pz$

Q. 11. Which of the following options represents the correct bond order:

(i) $O_2^- > O_2 > O_2^+$ **(ii)** $O_2^- < O_2 < O_2^+$

(iii) $O_2^- > O_2 < O_2^+$ **(iv)** $O_2^- < O_2 > O_2^+$

[NCERT Exemplar, Q. 20, Page 42]

Ans. Correct option : (ii)

Explanation : $O_2 = \sigma 1s^2\, \sigma^* 1s^2\, \sigma 2s^2\, \sigma^* 2s^2\, \pi 2px^2 = \pi 2py^2\, \pi^* 2px^1 = \pi^* 2py^1$

$$\text{Bond order} = \frac{10-6}{2} = 2$$

$O_2^- = \sigma 1s^2\, \sigma^* 1s^2\, \sigma 2s^2\, \sigma^* 2s^2\, \pi 2px^2 = \pi 2py^2\, \pi^* 2px^2 = \pi^* 2py^1$

$$\text{Bond order} = \frac{10-7}{2} = 1.5$$

$O_2^+ = \sigma 1s^2\, \sigma^* 1s^2\, \sigma 2s^2\, \sigma^* 2s^2\, \pi 2px^2 = \pi 2py^2\, \pi^* 2px^1 = \pi^* 2py^0$

$$\text{Bond order} = \frac{10-5}{2} = 2.5$$

Q. 12. Which the following have identical bond order?

(i) CN^- **(ii)** NO^+

(iii) O_2^- **(iv)** O_2^{2-}

[NCERT Exemplar, Q. 23, Page 43]

Ans. Correct option : (i) and (ii)

Explanation : CN^- (Number of electrons = 6 + 7 + 1 = 14)

NO^+ (Number of electrons = 7 + 8 – 1 = 14)

O_2^- (Number of electrons = 8 + 8 + 1 = 17)

O_2^{2-} (Number of electrons = 8 + 8 + 2 = 18)

Q. 13. Which of the following statements are correct about CO_3^{2-}?

(i) **The hybridisation of central atom is sp^3.**

(ii) **Its resonance structure has one C–O single bond and two C=O double bonds.**

(iii) **The average formal charge on each oxygen atom is 0.67 units.**

(iv) **All C–O bond lengths are equal.**

[NCERT Exemplar, Q. 27, Page 43]

Ans. Correct option : (iii) and (iv)

Explanation : The hybridisation of central atom is sp^2. Its resonance structure has two C – O single bond and one C = O double bonds.

Q. 14. Diamagnetic species are those which contain no unpaired electrons. Which among the following are diamagnetic?

(i) N_2 **(ii)** N_2^{2-}

(iii) O_2 **(iv)** O_2^{2-}

[NCERT Exemplar, Q. 28, Page 43]

Ans. Correct option : (i) and (iv)

Explanation : $N_2 = \sigma 1s^2\, \sigma^* 1s^2\, \sigma 2s^2\, \sigma^* 2s^2\, \pi 2px^2 = \pi 2py^2\, \sigma 2pz^2$

As it has no unpaired electron, hence, it is diamagnetic.

$N_2^{2-} = \sigma 1s^2\, \sigma^* 1s^2\, \sigma 2s^2\, \sigma^* 2s^2\, \pi 2px^2 = \pi 2py^2\, \sigma 2pz^2\, \pi^* 2px^1 = \pi^* 2py^1$

As it has two unpaired electrons, hence, it is paramagnetic.

O_2 = $\sigma 1s^2\ \sigma^*1s^2\ \sigma 2s^2\ \sigma^*2s^2\ \pi 2px^2 = \pi 2py^2\ \pi^*2px^1 = \pi^*2py^1$

As it has two unpaired electrons, hence, it is paramagnetic.

O_2^{2-} = $\sigma 1s^2\ \sigma^*1s^2\ \sigma 2s^2\ \sigma^*2s^2\ \pi 2px^2 = \pi 2py^2\ \pi^*2px^2 = \pi^*2py^2$

As it has no unpaired electrons, hence, it is diamagnetic.

Q. 15. Species having same bond order are:

(i) N_2 **(ii)** N_2^-

(iii) F_2^+ **(iv)** O_2^-

[NCERT Exemplar, Q. 29, Page 43]

Ans. Correct option : (iii) and (iv)

Explanation : N_2 : Bond order = $\frac{10-4}{2} = 3$

N_2^- : Bond order = $\frac{10-5}{2} = 2.5$

F_2^+ : Bond order = $\frac{10-7}{2} = 1.5$

O_2^- : Bond order = $\frac{10-7}{2} = 1.5$

Comprehension given below is followed by some multiple choice questions. Each question has one correct option. Choose the correct option.

Molecular orbitals are formed by the overlap of atomic orbitals. Two atomic orbitals combine to form two molecular orbitals called bonding molecular orbital (BMO) and antibonding molecular orbital (ABMO). Energy of anti- bonding orbital is raised above the parent atomic orbitals that have combined and the energy of the bonding orbital is lowered than the parent atomic orbitals. Energies of various molecular orbitals for elements hydrogen to nitrogen increase in the order:

$\sigma 1s < \sigma^*1s < \sigma 2s < \sigma^*2s < (\pi 2p_x = \pi 2p_y) < \sigma 2p_z < (\pi^*2p_x \approx \pi^*2p_y) < \sigma^*2p_z$ and for oxygen and fluorine, order of energy of molecular orbitals is given below :

$\sigma 1s < \sigma^*1s < \sigma 2s < \sigma^*2s < \sigma 2p_z < (\pi 2p_x \simeq \pi 2p_y) < (\pi^*2p_x \simeq \pi^*2p_y) < \sigma^*2p_z$

Different atomic orbitals of one atom combine with those atomic orbitals of the second atom which have comparable energies and proper orientation. Further, if the overlapping is head on, the molecular orbital is called 'Sigma', (σ) and if the overlap is lateral, the molecular orbital is called 'pi', (π). The molecular orbitals are filled with electrons according to the same rules as followed for filling of atomic orbitals. However, the order for filling is not the same for all molecules or their ions. Bond order is one of the most important parameters to compare the strength of bonds.

Q. 16. Which of the following statements is correct?

(i) In the formation of dioxygen from oxygen atoms, 10 molecular orbitals will be formed.

(ii) All the molecular orbitals in the dioxygen will be completely filled.

(iii) Total number of bonding molecular orbitals will not be same as total number of antibonding orbitals in dioxygen.

(iv) Number of filled bonding orbitals will be same as number of filled antibonding orbitals.

[NCERT Exemplar, Q. 65, Page 49]

Ans. Correct option : (i)

Explanation :

(ii) Two molecular orbitals of dioxygen contain unpaired electrons.

(iii) Total number of bonding molecular orbitals will be same as total number of antibonding orbitals in dioxygen.

(iv) Number of filled bonding orbitals will not always be same as number of filled antibonding orbitals.

Q. 17. Which of the following molecular orbitals has maximum number of nodal planes?

(i) σ^*1s

(ii) σ^*2p_z

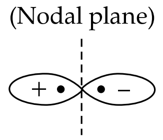
(iii) $\pi 2p_x$

(iv) π^*2p_y

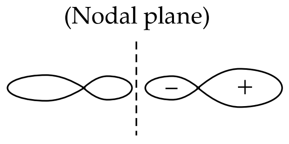
[NCERT Exemplar, Q. 66, Page 50]

Ans. Correct option : (iv)

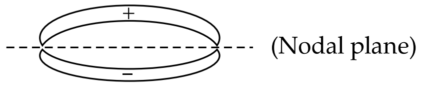
Explanation : σ^*1s, σ^*2p_z and $\pi 2p_x$ have one nodal plane while π^*2p_y has 2 nodal planes



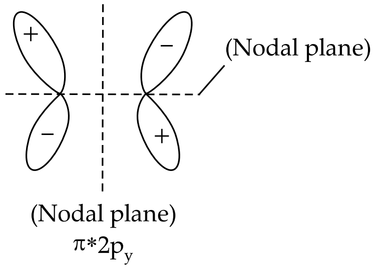
σ^*1s



σ^*2p_z



$\pi 2p_x$



π^*2p_y

Q. 18. Which of the following pair is expected to have the same bond order?

(i) O_2, N_2

(ii) O_2^+, N_2^-

(iii) O_2^-, N_2^+

(iv) O_2^-, N_2^-

[NCERT Exemplar, Q. 67, Page 50]

Ans. **Correct option :** (ii)

Explanation :	**Species**	**Bond order**
(i)	O_2	2.0
	N_2	3.0
(ii)	O_2^+	2.5
	N_2^-	2.5
(iii)	O_2^-	1.5
	N_2^+	2.5
(iv)	O_2^-	1.5
	N_2^-	2.5

Q. 19. In which of the following molecules, $\sigma 2p_z$ molecular orbital is filled after $\pi 2p_x$ and $\pi 2p_y$ molecular orbitals?

(i) O_2 **(ii)** Ne_2

(iii) N_2 **(iv)** F_2

[NCERT Exemplar, Q. 68, Page 50]

Ans. **Correct option :** (iii)

Explanation : In N_2, $\sigma 2p_z$ molecular orbital is filled after $\pi 2p_x$ and $\pi 2p_y$ molecular orbitals.

Assertion and Reason

(1 mark each)

In the following questions a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the choices given below each question.

Q. 1. Assertion (A): Though the central atom of both NH_3 and H_2O molecules are sp^3 hybridised, yet H–N–H bond angle is greater than that of H–O–H.

Reason (R): This is because nitrogen atom has one lone pair and oxygen atom has two lone pairs.

(i) A and R both are correct, and R is the correct explanation of A.

(ii) A and R both are correct, but R is not the correct explanation of A.

(iii) A is true but R is false.

(iv) A and R both are false.

[NCERT Exemplar, Q. 58, Page 48]

Ans. **Correct option :** (i)

Matching Type

(1 mark each)

Q. 1. Match the species in Column I with the type of hybrid orbitals in Column II.

Column I	**Column II**
(i) SF_4	(a) sp^3d^2
(ii) IF_5	(b) d^2sp^3
(iii) NO_2^+	(c) sp^3d
(iv) NH_4^+	(d) sp^3
	(e) sp

[NCERT Exemplar, Q. 52, Page 46]

Ans. (i) — (c), (ii) —a, (iii) –e, (iv) —d

Q. 2. Match the species in Column I with the geometry/shape in Column II.

Column I	**Column II**
(i) H_3O^+	(a) Linear
(ii) $HC \equiv CH$	(b) Angular
(iii) ClO_2^-	(c) Tetrahedral
(iv) NH_4^+	(d) Trigonal bipyramidal
	(e) Pyramidal

[NCERT Exemplar, Q. 53, Page 47]

Ans. (i) – e, (ii) – a, (iii) – b, (iv) – c

Q. 3. Match the species in Column I with the bond order in Column II.

Column I	**Column II**
(i) NO	(a) 1.5
(ii) CO	(b) 2.0
(iii) O_2^-	(c) 2.5
(iv) O_2	(d) 3.0

[NCERT Exemplar, Q. 54, Page 47]

Ans. (i) – c, (ii) – d, (iii) –a, (iv) – b

Q. 4. Match the items given in Column I with examples given in Column II.

Column I	**Column II**
(i) Hydrogen bond	(a) C
(ii) Resonance	(b) LiF
(iii) Ionic solid	(c) H_2
(iv) Covalent solid	(d) HF
	(e) O_3

[NCERT Exemplar, Q. 55, Page 47]

Ans. (i) – d, (ii) – e, (iii) – b, (iv) – a

Q. 5. Match the shape of molecules in Column I with the type of hybridisation in Column II.

Column I	**Column II**
(i) Tetrahedral	(a) sp^2
(ii) Trigonal	(b) sp
(iii) Linear	(c) sp^3

[NCERT Exemplar, Q. 56, Page 47]

Ans. (i) – c, (ii) – a, (iii) – b

Short Answer Type Questions **(3 marks each)**

Q. 1. Using molecular orbital theory, compare the bond energy and magnetic character of O_2^+ and O_2^- species.

[NCERT Exemplar, Q. 32, Page 44]

Ans. O_2^+ :

Electronic configuration :

$_8O = \overset{e-}{8} = 2, 6 = 1s^2, 2s^2, 2p^4$

$_8O^+ = 7 = 2, 5 = 1s^2, 2s^2, 2p^3$

Molecular orbital configuration:

$(\sigma 1s)^2, (\sigma^*1s)^2, (\sigma 2s)^2, (\sigma^*2s)^2, (\sigma 2p_z)^2, (\pi 2p_x)^2$

$= (\pi 2p_y)^2, (\sigma^*2p_x)^1 = (\pi^*2p_y)^0\, (\sigma^*2p_z)^0$

$$\text{Bond order} = \frac{n_b - n_a}{2} = \frac{10-5}{2} = \frac{5}{2} = 2.5$$

O_2^- :

Electronic configuration :

$_8O^- = \overset{e-}{9} = 2, 7 = 1s^2, 2s^2 2p^5$

$_8O = 8 = 2, 6 = 1s2^2p^22p^4$

Molecular orbital configuration :

$(\sigma 1s)^2, (\sigma^*1s)^2\, (\sigma 2s)^2\, (\sigma^*2s)^2, (\sigma 2p_z)^2, (\pi 2p_x)^2 =$

$(\pi 2p_y)^2, (\pi^*2p_x)^2 = (\pi^*2p_y)^1\, (\sigma^*2p_z)^0$

$$\text{Bond order} = \frac{n_b - n_b}{2}$$

$$= \frac{10-7}{2} = \frac{3}{2} = 1.5$$

According to molecular orbital theory,

Bond order α bond energy

Greater the bond order of molecule or ion, greater will be the bond energy of that molecule or ion.

$\because$ O_2^+ has higher bond order (2.5) than O_2^- (1.5), so, the bond energy of O_2^+ is higher than O_2^-. Hence, O_2^+ is more stable then O_2^-.

Since both ions have unpaired electron in molecular orbitals, so both are paramagnetic in nature.

Q. 2. Explain the shape of BrF_5.

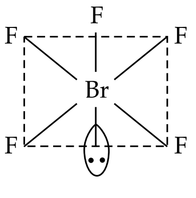
[NCERT Exemplar, Q. 33, Page 44]

Ans. BrF_5

$_{35}Br = 2, 8, 18, 7$

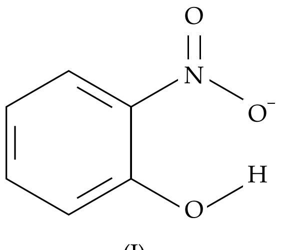
$= 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^5$

In BrF_5 , the central atom Br contains 7 valence electrons. Out of which, five electrons are used to make bonds with five F-atoms and the remaining two electrons are present as one lone pair. Its structure is shown as below:

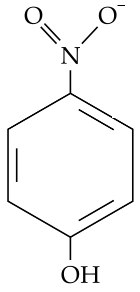


Due to lp-bp repulsion, the shape of BrF_5 is distorted i.e. square pyramidal.

Q. 3. Structures of molecules of two compounds are given below:



(I)



(II)

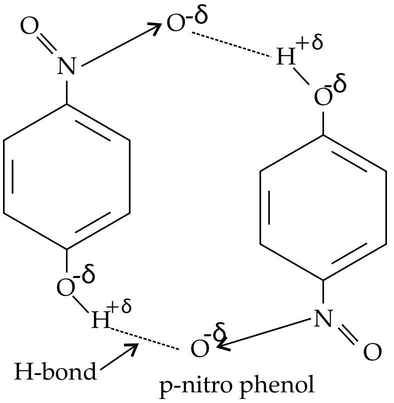
(a) Which of the two compounds will have intermolecular hydrogen bonding and which compound is expected to show intramolecular hydrogen bonding?

(b) The melting point of a compound depends on, among other things, the extent of hydrogen bonding. On this basis, explain which of the above two compounds will show higher melting point.

(c) Solubility of compounds in water depends on power to form hydrogen bonds with water. Which of the above compounds will form hydrogen bond with water easily and be more soluble in it?

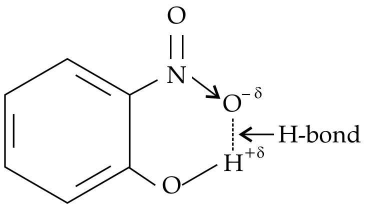
[NCERT Exemplar, Q. 34, Page 44]

Ans. (a) Compound (II) will have intermolecular hydrogen bonding, because –NO_2 and –OH groups are attached at 1, 4 positions. So, two molecules of compound (II) i.e. p-nitrophenol are joined by intermolecular hydrogen bonding.



p-nitro phenol

Compound (I) will have intramolecular hydrogen bonding because –NO_2 and –OH groups are attached at 1, 2 positions. So, H-bonding takes place in same molecule i.e. o-nitrophenol.

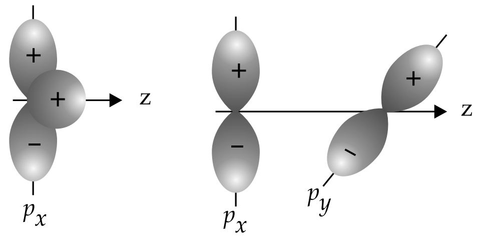


o-nitrophenol

(b) Compound (II) will show higher melting point because large number of molecules are joined together by intermolecular hydrogen bonding.

(c) Compound (II) will form hydrogen bond with water easily so it is more soluble in water. However, compound (I) exhibits intra-molecular hydrogen bonding so it is not able to form H-bond with water and it is less soluble in water.

Q. 4. Why does type of overlap given in the following figure not result in bond formation?



[NCERT Exemplar, Q. 35, Page 45]

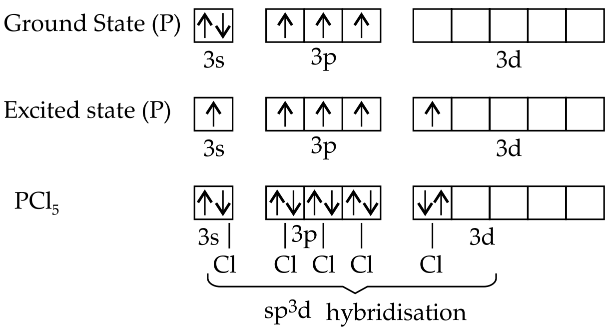
Ans. In first figure, area of ++ overlap is equal to area of +– overlap. So, net overlap is zero. Whereas in second figure, there is no overlap due to different symmetry.

Q. 5. Explain why PCl_5 is trigonal bipyramidal where as IF_5 is square pyramidal?

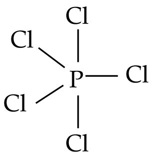
[NCERT Exemplar, Q. 36, Page 45]

Ans. PCl_5 : ${}_{15}P$ = 2, 8, 5

$= 1s^2, 2s^22p^6, 3s^23p^3$

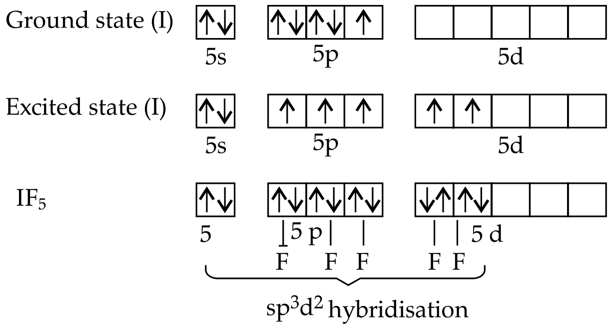


In PCl_5, the central atom contains five valence electrons. All these electrons are used to form bond with five Cl-atoms. So, there is no lone pair present in PCl_5. It possesses sp^3d hybridisation. So, its shape in trigonal bipyramidal. Its structure is shown as below:

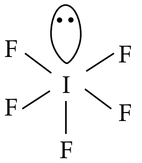


IF_5: ${}_{53}I$ = 2, 8, 18, 18, 7

$= 1s^2, 2s^22p^6, 3s^23p^63d^{10}, 4s^24p^64d^{10}, 5s^25p^5$



In IF_5, the central atom contains 7 valence electrons. Out of which, 5 electrons are used to form bonds with five fluorine atoms. The remaining two electrons are present as one lone pair. It possesses sp^3d^2 hybridisation. But, due to lp-bp repulsion, shape of IF_5 is distorted i.e. square pyramidal. Its structure is shown as below:



Q. 6. The energy of $\sigma 2p_z$ molecular orbital is greater than $\pi 2p_x$ and $\pi 2p_y$ molecular orbitals in nitrogen molecule. Write the complete sequence of energy levels in the increasing order of energy in the molecule. Compare the relative stability and the magnetic behaviour of the following species :

N_2, N_2^+, N_2^-, N_2^{2+}

[NCERT Exemplar, Q. 39, Page 45]

Ans. The complete sequence of energy levels in the increasing order of energy in nitrogen molecule/ ion is:

$(\sigma 1s), (\sigma^*1s), (\sigma 2s), (\sigma^*2s), (\pi 2p_x)$
$= (\pi 2p_y), (\sigma 2p_z), (\pi^*2p_x) = (\pi^*2p_y), (\sigma^*2p_z)$

N_2 : Electronic configuration

${}_7\mathbf{N}$ = 7 = 2, 5 = $1s^2, 2s^22p^3$

${}_7\mathbf{N}$ = 7 = 2, 5 = $1s^2, 2s^22p^3$

Total electrons present = 14

Molecular orbital configuration:

$(\sigma 1s)^2, (\sigma^*1s)^2, (\sigma 2s)^2, (\sigma^*2s)^2, (\pi 2p_x)^2$
$= (\pi 2p_y)^2, (\sigma 2p_z)^2, (\pi^*2p_x)^0 = (\pi^*2p_y)^0,$
$(\sigma^*2p_z)^0$

Bond order = $\frac{N_b - N_a}{2} = \frac{10-4}{2} = \frac{6}{2} = 3$

∴ There is no unpaired electron present in molecular orbitals of N_2 molecule, so it is diamagnetic in nature.

N_2^+ (Lost of one electron due to +ve charge)

∴ Total electrons present = 14 – 1 = 13

M.O. configuration:

$(\sigma 1s)^2, (\sigma^* 1s)^2, (\sigma 2s)^2, (\sigma^* 2s)^2, (\pi 2p_x)^2 = (\pi 2p_y)^2, (\sigma 2p_z)^1, (\pi 2p_x)^0 = (\pi^* 2p_y)^0, (\sigma^* 2p_z)^0$

Bond order = $\dfrac{N_b - N_a}{2} = \dfrac{9-4}{2} = \dfrac{5}{2} = 2.$

∴ There is one unpaired electron present in molecular orbital of N_2^+ molecular ion, so it is paramagnetic in nature.

N_2^- (Gain of one election due to –ve charge)

∴ Total electrons present = 14 + 1 = 15

M.O. configuration :

$(\sigma 1s)^2, (\sigma^* 1s)^2, (\sigma 2s)^2, (\sigma^* 2s)^2, (\pi 2p_x)^2 = (\pi 2p_y)^2, (\sigma 2p_z)^2, (\pi^* 2p_x)^1 = (\pi^* 2p_y)^0, (\sigma^* 2p_z)^0$

Bond order = $\dfrac{N_b - N_a}{2} = \dfrac{10-5}{2} = \dfrac{5}{2} = 2.$

∴ There is one unpaired electron present in molecular orbital of N_2^- ion, so it is paramagnetic in nature.

N_2^{2+} (Loss of two electrons due to double +ve charge)

∴ Total electrons present = 14 – 2 = 12

M.O. configuration :

$(\sigma 1s)^2, (\sigma^* 1s)^2, (\sigma 2s)^2, (\sigma^* 2s)^2, (\pi 2p_x)^2 = (\pi 2p_y)^2, (\sigma 2p_z)^0, (\pi 2p_x)^0 = (\pi^* 2p_y)^0, (\sigma^* 2p_z)^0$

Bond order = $\dfrac{N_b - N_a}{2} = \dfrac{8-4}{2} = \dfrac{4}{2} = 2$

∴ There is no unpaired electron present in molecular orbital of N_2^+ ion, so it is diamagnetic in nature.

Since, bond order α stability of molecular/ion.

So, Relative order of stability is :

$$N_2 > N_2^- \approx N_2^+ > N_2^{2+}$$

(most stable) (least stable)

Q. 7. What is the effect of the following processes on the bond order in N_2 and O_2?

(a) $N_2 \longrightarrow N_2^+ + e^-$

(b) $O_2 \longrightarrow O_2^+ + e^-$

[NCERT Exemplar, Q. 40, Page 45]

Ans. According to molecular orbital theory, bond orders of N_2, O_2, N_2^+ and O_2^+ are calculated as follow:

N_2 (Total electrons = 14)

M.O. Configuration:

$(\sigma 1s)^2, (\sigma^* 1s)^2, (\sigma 2s)^2, (\sigma^* 2s)^2, (\pi 2p_x)^2 = (\pi 2p_y)^2, (\sigma 2p_z)^2 \ (\pi^* 2p_x)^0 = (\pi^* 2p_y)^0, (\sigma^* 2p_z)^0$

Bond order = $\dfrac{N_b - N_a}{2} = \dfrac{10-4}{2} = 3$

N_2^+ (Total electrons = 14 – 1 = 13)

M.O. Configuration :

$(\sigma 1s)^2, (\sigma^* 1s)^2, (\sigma 2s)^2, (\sigma^* 2s)^2, (\pi 2p_x)^2 = (\pi 2p_y)^2 (\sigma 2p_z)^1, (\pi^* 2p_x)^0 = (\pi^* 2p_y)^0, (\sigma^* 2p_z)^0$

Bond order = $\dfrac{N_b - N_a}{2} = \dfrac{9-4}{2} = 2.5$

O_2 (Total electrons = 16)

M.O. Configuration :

$(\sigma 1s)^2, (\sigma^* 1s)^2, (\sigma 2s)^2, (\sigma^* 2s)^2, (\sigma 2p_z)^2 = (\pi 2p_x)^2 = (\pi 2p_y)^2, (\pi^* 2p_x)^1 = (\pi^* 2p_y)^1, (\sigma^* 2p_z)^0$

Bond order = $\dfrac{N_b - N_a}{2} = \dfrac{10-6}{2} = 2$

O_2^+ (Total electrons = 16 – 1 = 15)

M.O. Configuration :

$(\sigma 1s)^2, (\sigma^* 1s)^2, (\sigma 2s)^2, (\sigma^* 2s)^2, (\sigma 2p_z)^2$ $(\pi 2p_x)^2 = (\pi 2p_y)^2, (\pi^* 2p_x)^1 = (\pi^* 2p_y)^0, (\sigma^* 2p_z)^0$

Bond order = $\dfrac{N_b - N_a}{2} = \dfrac{10-5}{2} = 2.5$

(a) $N_2 \longrightarrow N_2^+ + e^-$

Bond order 3.0 2.5

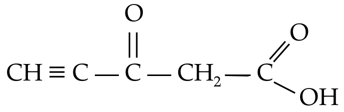
∴ The bond order decreases in this process.

(b) $O_2 \longrightarrow O_2^+ + e^-$

Bond order 2.0 2.5

∴ The bond order increases in this process.

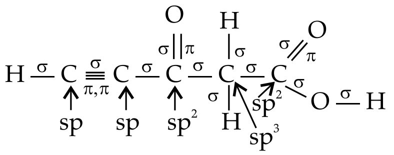
Q. 8. Predict the hybridisation of each carbon in the molecule of organic compound given below. Also indicate the total number of sigma and pi bonds in this molecule.



$$CH \equiv C - \overset{\overset{O}{\|}}{C} - CH_2 - C\!\begin{smallmatrix} \nearrow O \\ \searrow OH \end{smallmatrix}$$

[NCERT Exemplar, Q. 45, Page 46]

Ans.



Total number of sigma bonds = 11

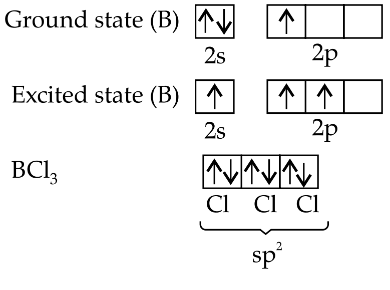
Total number of pi bonds = 4

Q. 9. Predict the shapes of the following molecules on the basis of hybridisation.

BCl_3, CH_4, CO_2, NH_3

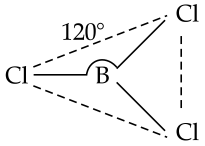
[NCERT Exemplar, Q. 49, Page 46]

Ans. BCl_3 : $_5B$ = 2, 3 = $1s^2, 2s^2 2p^1$



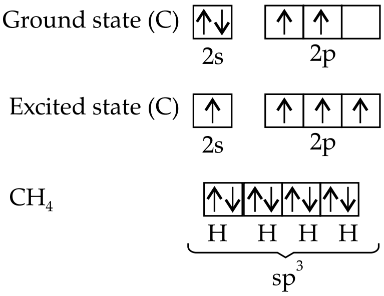
Since, BCl_3 possesses sp^2 hybridisation. So, its shape is **trigonal planar** with bond angle of 120°.

The structure of BCl_3 is shown as below:



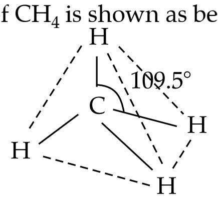
Structure of BCl_3

CH_4 : ${}_6C = 2, 4 = 1s^2, 2s^2 2p^2$



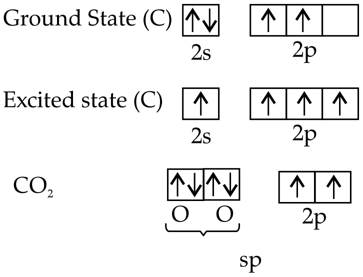
Since, CH_4 possesses sp^3 hybridisation with four bond pairs and zero lone pairs. So, its shape is **tetrahedral** with bond angle of 109.5°.

The structure of CH_4 is shown as below :



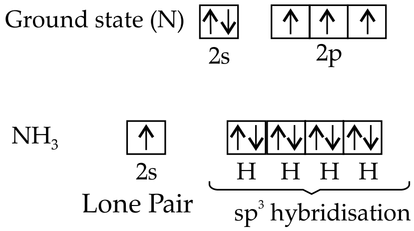
Structure of CH_4

CO_2 : ${}_6C = 2, 4 = 1s^2, 2s^2 2p^2$

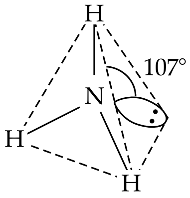


Since CO_2 possesses sp hybridisation. So, its shape is **linear** with bond angle of 180°.

NH_3 : ${}_7N = 2, 5 = 1s^2, 2s^2 2p^3$



Since, NH_3 possesses sp^3 hybridisation with three bond pairs and one lone pair of electrons. Due to lp–lp repulsion, the shape of NH_3 is pyramidal with bond angle of 107°.



(Structure of NH_3)

Long Answer Type Questions **(5 marks each)**

Q. 1. Use the molecular orbital energy level diagram to show that N_2 would be expected to have a triple bond, F_2, a single bond and Ne_2, no bond.

[NCERT Exemplar, Q. 61, Page 48]

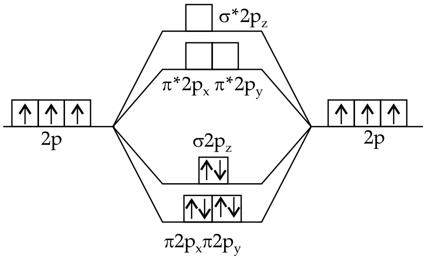
Ans. N_2 (Total electrons = 7 + 7 = 14)

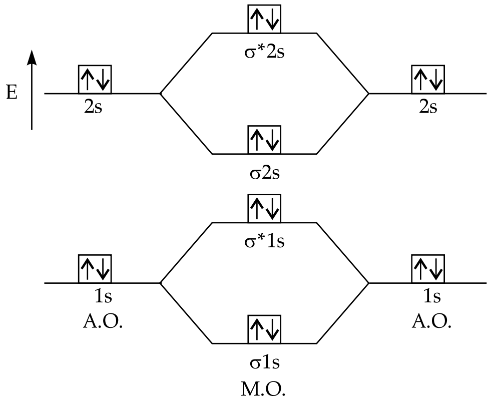
$$\left\{\begin{array}{l} {}_7N = 2, 5 = 1s^2, 2s^2 2p^3 \\ {}_7N = 2, 5 = 1s^2, 2s^2 2p^3 \end{array}\right\}$$

Molecular Orbital Configuration:

$(\sigma 1s)^2, (\sigma^* 1s)^2, (\sigma 2s)^2, (\sigma^* 2s)^2, (\pi 2p_x)^2 = (\pi 2p_y)^2, (\sigma 2p_z)^2, (\pi 2p_x)^0 = (\pi^* 2p_y)^0, (\sigma^* 2p_z)^0$

Molecular orbital energy level diagram :





Bond order $= \dfrac{N_b - N_a}{2} = \dfrac{10-4}{2} = \dfrac{6}{2} = 3$

Since, the bond order of N_2 is 3, so N_2 has a triple bond. ($N \equiv N$)

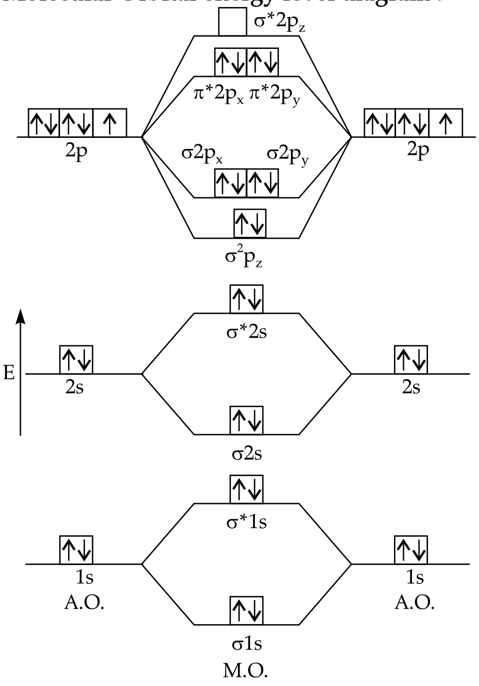
F_2 : (Total electrons = 9 + 9 = 18)

$$\left\{\begin{array}{l} {}_9F = 2, 7 = 1s^2, 2s^2 2p^5 \\ {}_9F = 2, 7 = 1s^2, 2s^2 2p^5 \end{array}\right\}$$

Molecular Orbital Configuration :

$(\sigma 1s)^2$, $(\sigma^* 1s)^2$, $(\sigma 2s)^2$, $(\sigma^* 2s)^2$, $(\sigma 2p_z)^2$ $(\pi 2p_x)^2$ $= (\pi 2p_y)^2$, $(\pi^* 2p_x)^2 = (\pi^* 2p_y)^2$,$(\sigma^* 2p_z)^0$

Molecular Orbital energy level diagram :



Bond order $= \frac{N_b - N_a}{2} = \frac{10-8}{2} = \frac{2}{2} = 1$

Since, the bond order of F_2 is 1 so F_2 has a single bond. (F – F)

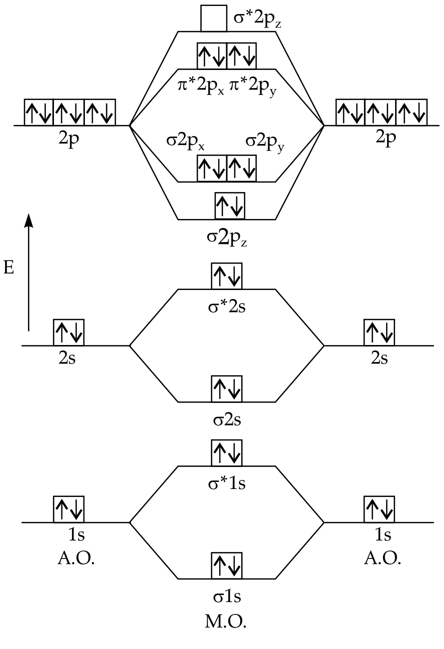
Ne_2 : (Total electrons = 20)

$$\left\{\begin{matrix} {}_{10}\text{Ne} = 2, 8 = 1s^2, 2s^2 2p^6 \\ {}_{10}\text{Ne} = 2, 8 = 1s^2, 2s^2 2p^6 \end{matrix}\right\}$$

Molecular Orbital Configuration :

$(\sigma 1s)^2$, $(\sigma^* 1s)^2$, $(\sigma 2s)^2$, $(\sigma^* 2s)^2$, $(\sigma 2p_z)^2$, $(\pi 2p_x)^2 = (\pi 2p_y)^2$, $(\pi^* 2p_x)^2 = (\pi^* 2p_y)^2$, $(\sigma^* 2p_z)^2$

Molecular orbital Energy profile diagram.



Bond order $= \frac{N_b - N_a}{2} = \frac{10-10}{2} = \frac{0}{2} = 0$

Since, the bond order of Ne_2 is zero, so, Ne_2 would be expected to have no bond i.e. it does not exist as a molecule.

Q. 2. Briefly describe the valence bond theory of covalent bond formation by taking an example of hydrogen. How can you interpret energy changes taking place in the formation of dihydrogen?

[NCERT Exemplar, Q. 62, Page 48]

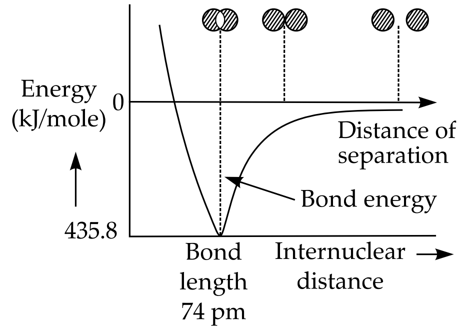
Ans. Consider two hydrogen atoms A and B having one electron in its 1s subshell. These atoms approach each other having nuclei N_A and N_B and electrons present in them are represented by e_A and e_B. When the two atoms are at large distance from each other, there is no interaction between them. As these atoms begin to approach each other, new attractive and repulsive forces begin to operate.

(i) Attractive forces arise between nucleus of A and electron of B and vice-versa i.e. $N_A - e_B$, $N_B - e_A$ or $N_A - e_B$, $N_B - e_A$.

(ii) Repulsive forces arise between nuclei of two atoms A and B i.e. $N_A - N_B$.

(iii) Repulsive forces arise between electrons of two atoms A and B i.e. $e_A - e_B$

Attractive forces tend to bring the two atoms close to each other while repulsive forces tend to push them apart.



P.E. curve for the formation of H_2 molecule

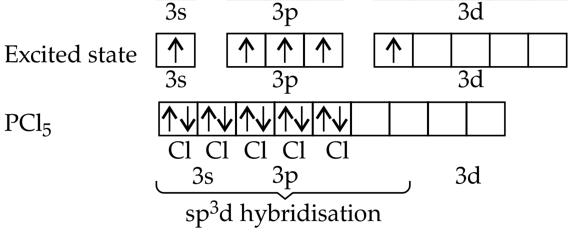
It has been found that the magnitude of new attractive forces is more than the new repulsive forces. As a result, two atoms approach each other and potential energy decreases. Further, a stage is reached where the net force of attractive balances the force of repulsion and system acquires minimum energy. At this stage, the two hydrogen atoms are said to be bonded together to form a stable molecule having the bond length of 74 pm.

The energy released in the formation of H_2 molecule is called bond enthalpy, which corresponds to the minimum in the curve represented in above figure. 435.8 kJ of energy is required to dissociate one mole of H_2 molecule.

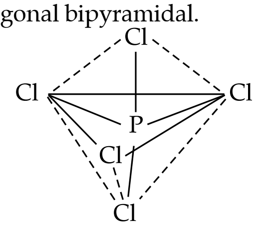
Q. 3. Describe hybridisation in the case of PCl_5 and SF_6. The axial bonds are longer as compared to equatorial bonds in PCl_5 whereas in SF_6 both axial bonds and equatorial bonds have the same bond length. Explain.

[NCERT Exemplar, Q. 63, Page 48]

Ans. ${}_{15}P$ = 2, 8, 5 = $1s^2, 2s^2\,2p^6, 3s^2 3p^3$



Five orbitals *i.e.* one s, three p and one d-orbitals are available for hybridisation to form five sp^3d hybrid orbitals in the formation of PCl_5. These five sp^3d hybrid orbitals are directed towards the five corners of trigonal bipyramidal.



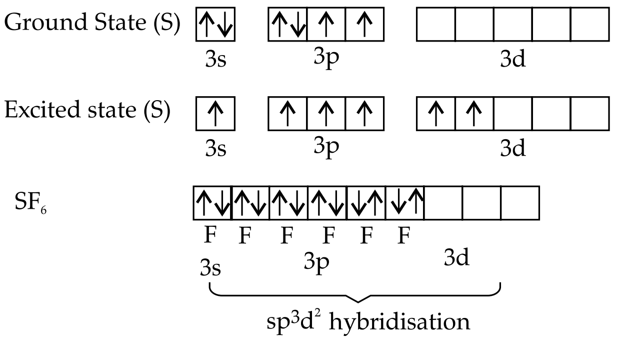
(Trigonal bipyramidal shape of PCl_5)

All the bond angles in this structure are not equivalent. In PCl_5, three P-Cl bonds lie in one plane with bond angle of 120°. These bonds are called equatorial bonds. The remaining two P-Cl bonds, one lying above and other lying below the equatorial plane form an angle of 90° with the plane. These bonds are called axial bonds.

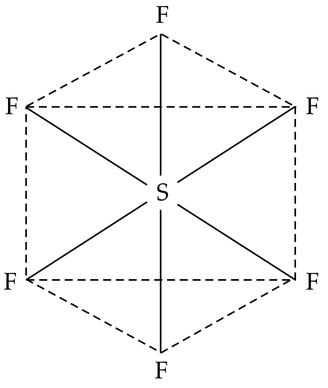
Axial bonds are longer as compared to the equatorial bonds due to great repulsion on axial bond pair electrons by equatorial bond pair electrons.

SF_6 : ${}_{16}S$ = 2, 8, 6

= $1s^2, 2s^2 2p^6, 3s^2 3p^4$



∴ SF_6 possesses sp^3d^2 hybridisation. In SF_6, the central atom S contains six valence electrons. All these electrons are used to form bonds with six F-atoms. So, its shape is octahedral and all S-F bonds i.e. axial and equatorial bonds have the same bond length. Its structure is shown as below.

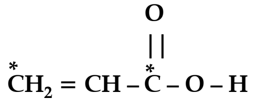


(SF_6)

Q. 4. (i) Discuss the concept of hybridisation. What are its different types in a carbon atom?

(ii) What is the type of hybridisation of carbon atoms marked with star?

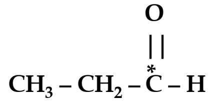
(a)



$$\overset{*}{C}H_2 = CH - \overset{*}{\underset{}{C}}(=O) - O - H$$

(b) $CH_3 - \overset{*}{C}H_2 - OH$

(c)



$$CH_3 - CH_2 - \overset{*}{C}(=O) - H$$

(d) $\overset{*}{C}H_3 - CH = CH - CH_3$

(e) $CH_3 - \overset{*}{C} \equiv CH$

[NCERT Exemplar, Q. 64, Page 48]

Ans. (i) Hybridisation : It is defined as the process of intermixing of the orbitals of slightly different energy or of same energy to form entirely new orbitals of equivalent energy and shape called hybrid orbitals. The orbitals present in the valence shall of the atom are hybridised. The orbitals undergoing hybridisation should have almost equal energy. Hybrid orbitals do not form π-bonds.

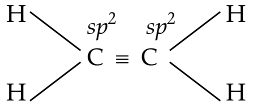
The different types of hybridisation present in carbon atom are given as below :

(a) sp-Hybridisation : This type of hybridisation is found in compounds of carbon having C ≡ C triple bonds.

e.g. H—$\overset{sp}{C} \equiv \overset{sp}{C}$—H.

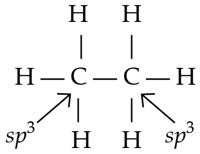
(b) sp^2-Hybridisation : This type of hybridization is found in compounds of carbon having C = C double bond.

e.g.

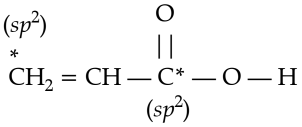


(c) sp^3 Hybridisation : This type of hybridisation is found in compounds of carbon having C – C single bond.

e.q.

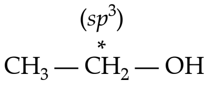


(ii) (a)



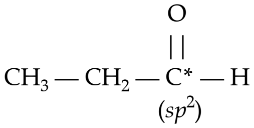
$$\overset{(sp^2)}{\overset{*}{CH_2}} = CH - \underset{(sp^2)}{\overset{\overset{O}{||}}{C^*}} - O - H$$

(b)



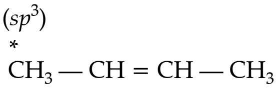
$$CH_3 - \overset{(sp^3)}{\overset{*}{CH_2}} - OH$$

(c)



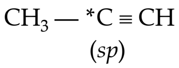
$$CH_3 - CH_2 - \underset{(sp^2)}{\overset{\overset{O}{||}}{C^*}} - H$$

(d)



$$\overset{(sp^3)}{\overset{*}{CH_3}} - CH = CH - CH_3$$

(e)



$$CH_3 - \underset{(sp)}{{}^*C} \equiv CH$$

* * *