# 4

# Chemical Bonding and Molecular Structure

*Chemical bonding is extremely important in everyday life. You've probably heard of gasoline, LPG, CNG, and other fuels. These are the types of fuels that will allow you to continue your long journey. Using the proper oil to fuel your vehicle ensures that it performs optimally. The fuel or gases that are used in vehicles are the results of atom bonding.*

## Topic Notes

- *Chemical Bonding*
- *Bond Parameters*
- *Theories of Chemical Bonding*
- *Hybridisation and Molecular Orbital Theory*
- *Hydrogen Bonding*

# CHEMICAL BONDING 1

## TOPIC 1

## CHEMICAL BONDING

We can't live in isolation; and people like to form bonds with one another. People may form strong bonds with one another, and some atoms can form strong bonds with one another as well. Weak connections can exist between atoms, just as they might exist between two people.

Chemical bonding between atoms creates the proteins we require and the carbohydrates we consume. Chemical bonding is responsible for the gas we utilize in our cars. We breathe oxygen ($O_2$) as a result of a chemical connection. Chemical bonding between atoms produces the medicines we need to heal ourselves. When two atoms or molecules are held together in different chemical species, there is a certain chemical link between them which is termed as a chemical bond. These bonds are the forces of attraction between two atoms or molecules. They are formed to increase stability with the emancipation of energy.

### Kossel – Lewis Approach to Chemical Bond

A logical explanation for chemical bonding was provided by Kossel and Lewis in 1916. Their approach to chemical bonding is based on the inertness of the noble gases which have little or no tendency to combine with other atoms. They proposed that the noble gases are stable due to their completely filled outer shell electronic configuration. According to this method, atoms take part in bond formation to achieve the nearest noble gas electronic configuration. In other words, atoms form bonds to complete their octet or duplet to have the nearest stable noble gas configuration. The bond is formed by losing, gaining or sharing one or more electrons from their outer shell. For example, sodium loses one electron to form $Na^+$ ion and chlorine accepts that electron to give chloride ion ($Cl^-$), enabling both atoms to attain the nearest noble gas configuration. The resultant ions, $Na^+$ and $Cl^-$ are held together by electrostatic attractive forces and the attractive force is called a chemical bond.

### Facts of Kossel Lewis Theory

In the periodic table, the highly electronegative halogens and the highly electropositive alkali metals are separated by the noble gases.

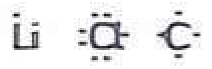
(1) The formation of a negative ion from a halogen atom and a positive ion from an alkali metal atom is associated with the gain and loss of an electron by the respective atoms.

(2) The negative and positive ions thus formed attain stable noble gas electronic configurations. The noble gases (with the exception of helium which has a duplet of electrons) have a particularly stable outer shell configuration of eight (octet) electrons, $ns^2np^6$.

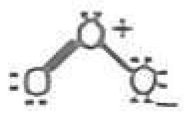
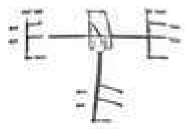
(3) The negative and positive ions are stabilised by electrostatic attraction.

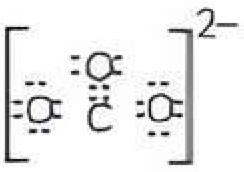
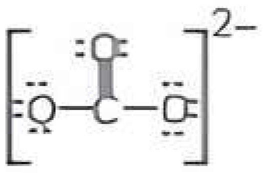
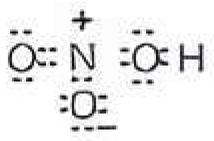
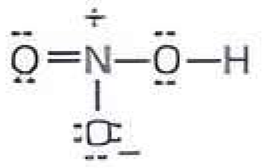
### Lewis Symbols

In 1916, Lewis introduced simple symbols to represent valence shell electrons of the atom these simple symbols are known as Lewis Symbol. The Lewis symbol is the chemical symbol of elements where the valence electrons are represented as the dots. For example,



These symbols help to calculate the common or group valence of the element. The group valence of the element is either equal to the number of dots or 8 minus the number of dots.

| Molecule/ Ion | Lewis Representation | |
|---|---|---|
| $H_2$ | H : H | H – H |
| $O_2$ | $:\ddot{O}::\ddot{O}:$ | $:\ddot{O}=\ddot{O}:$ |
| $O_3$ |  |  |
| $NF_3$ |  |  |

| Molecule/ Ion | Lewis Representation | |
|---|---|---|
| $CO_3^{2-}$ |  |  |
| $HNO_3$ |  |  |

## Lewis Representation of Simple Molecules (Lewis Structures)

The Lewis dot structures provide a picture of bonding in molecules and ions in terms of the shared pairs of electrons and the octet rule. Following rules should be adopted while writing Lewis structures:

(1) The total number of electrons required for writing the structures is obtained by adding the valence electrons of the combining atoms.

(2) For anions, each negative charge would mean the addition of one electron. For cations, each positive charge would result in subtraction of one electron from the total number of valence electrons.

(3) Knowing the chemical symbols of the combining atoms and having knowledge of the skeletal structure of the compound (known or guessed intelligently), it is easy to distribute the total number of electrons as bonding shared pairs between the atoms in proportion to the total bonds.

(4) In general the least electronegative atom occupies the central position in the molecule/ion.

(5) After accounting for the shared pairs of electrons for single bonds, the remaining electron pairs are either utilized for multiple bonding or remain as the lone pairs. The basic requirement being that each bonded atom gets an octet of electrons.

**Example 1.1: Write the Lewis dot structure of CO molecule. [NCERT]**

**Ans. Step 1:** Firstly, we have to count the total number of valence shell electrons of both carbon and oxygen atoms. The electronic configuration of carbon and oxygen atoms in their outer shells:

$C = 2s^2 2p^2$

$O = 2s^2 2p^4$

The valence electrons are therefore

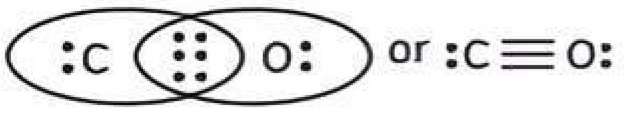
$4 + 6 = 10$

**Step 2:** CO's skeletal structure is written as:

C O

**Step 3:** Draw the valence electrons as dots and represent one shared electron pair as a single bond while the remaining electron pairs as lone pairs :C——$\ddot{\underset{..}{O}}$:

But still, the octet of carbon does not complete so we have to use multiple bonding between carbon and oxygen atoms which satisfies the octet rule for both atoms.



**Example 1.2: Write the Lewis structure of the nitrite ion, $NO_2^-$. [NCERT]**

**Ans. Step 1:** Firstly, we have to count the total number of valence shell electrons of both nitrogen and oxygen atoms. The outer shell electronic configuration of nitrogen and oxygen atoms and the molecule contains one additional negative charge.

$N = 2s^2 2p^3$

$O = 2s^2 2p^4$

Thus, the valence electrons are

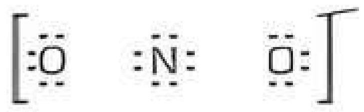
$= 5 + (2 \times 6) + 1$

$= 18$ electrons

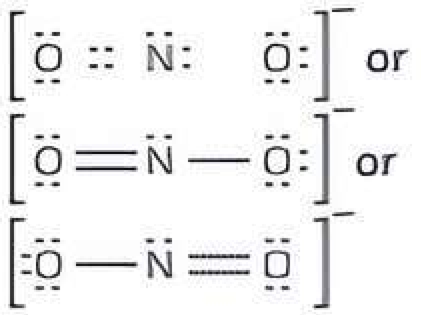
**Step 2:** Write the skeletal structure of $NO_2^-$ as:

O N O

**Step 3.** Draw the valence electrons as dots and represent one shared electron pair as a single bond for completing the octet of both atoms while remaining electron pairs as lone pairs. But by doing this the octet of nitrogen does not complete if the remaining two electrons form lone pairs on it.



So, we have to use multiple bonds between nitrogen and oxygen atoms which satisfies the octet rule for both the atoms.



## Octet Rule

The octet rule has these significant drawbacks:

(1) The form of the molecule cannot be anticipated according to this criterion.

(2) This criterion cannot determine a molecule's relative stability.

### Limitations of the Octet Rule

There are mainly two limitations of the octet rule:

(1) The incomplete octet of the central atom

(2) Any bond is not completely ionic or completely covalent. when the octet rule is applied to some molecules which have almost equal ionic and covalent characteristics. this rule fails.

**For example:** In some polyatomic molecules like LiCl. $BeH_2$ and $BCl_3$. the number of electrons surrounding the central atom is less than eight. Li. Be and B have 1.2 and 3 valence electrons only. This is especially the case with elements having less than four electrons in their valence shell. Examples of other such compounds are $AlCl_3$ and $BF_3$.

**Odd-electron molecules**

Molecules having an odd number of electrons like nitric oxide. NO and nitrogen dioxide. $NO_2$. do not satisfy the octet rule for all the atoms.

**The expanded octet**

Elements in the third period of the periodic table and beyond have 3*d* orbitals. (apart from 3s and 3*p* orbital) available for bonding. As we know that the atom will be stable when the outermost shell is completely filled. In this case (4th period) the completely filled outermost shell can accommodate 18 electrons. Numerous compounds of these elements have more than eight valence electrons around the central atom. This is termed as the expanded octet. Some examples of such compounds are: $PF_5$. $SF_6$. $H_2SO_4$ and number of coordination compounds.

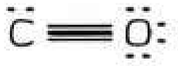
**Example 1.3:** Case Based:

*Lewis structures are illustrations that illustrate the bonding between atoms in a molecule. and just about any lone pairs of electrons that could be present. They are also characterized as Lewis dot formulae. Lewis dot structures. electron dot structures. as well as Lewis electron dot structures (LEDS). A Lewis structure can represent any covalently linked molecule. but also coordination compounds. Gilbert N. Lewis introduced the Lewis structure in his 1916 essay. The Atom and the Molecule. and it was named after him. Lewis structures add lines between atoms to indicate shared pairs in a chemical bond. extending the notion of the electron dot diagram.*

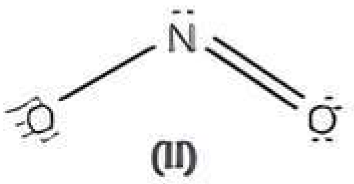
**(A) Among the following which molecule possess a full octet of the central atom, according to the Lewis and Kossel approach?**

**(a) LiCl (b) $BeH_2$**
**(c) $BCl_3$ (d) $CO_2$**

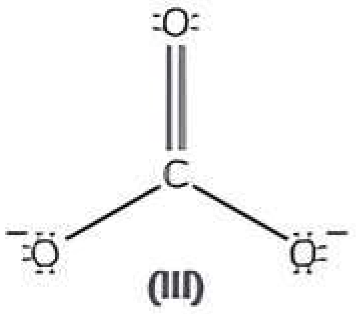
**(B) CO, $NO_2^-$, and $CO_3^{2-}$ have the following Lewis dot structures of I, II and III, respectively.**



(I)



(II)



(III)

**Which of the structures listed above is/are incorrect?**

**(a) Only (I) (b) Only (II)**
**(c) Only (III) (d) All of the these**

**(C) Draw Lewis structure of $CN^-$.**

**(D) Assertion (A): $SF_6$, $PCl_5$, $H_2SO_4$ etc, are the compounds having incomplete octets.**

**Reason (R): As they contain more than eight electrons.**

**(a) Both (A) and (R) are true and (R) is the correct explanation of (A).**

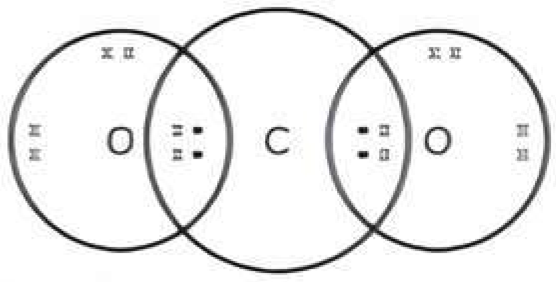
**(b) Both (A) and (R) are true but (R) is not the correct explanation of (A).**

**(c) (A) is true but (R) is false.**

**(d) (A) is false but (R) is true.**

**Ans. (A)** *(d) $CO_2$*

**Explanation:** According to Lewis and Kossel's method. the $CO_2$ molecule possesses a full octet of the central atom. molecules containing an incomplete octet of core atoms include LiCl. $BeH_2$. and $BCl_3$. The Lewis structure of $CO_2$ is as follows:



**(B)** *(a) Only (I)*

**Explanation:** The Lewis dot structure of CO (I) is incorrect. Its correct structure is drawn as follows:

:C = O:

**(C)** The Lewis structure of $CN^-$ is

$[:C = N:]^-$

**(D)** *(d) (A) is false but (R) is true.*

**Explanation:** In $PF_5$. $SF_6$ and $H_2SO_4$. the central atom has more than eight valence electrons. Hence. they exhibit an expanded octet. not an incomplete octet. This is possible due to the availability of 3d orbitals. Elements in and beyond the third period of the periodic table do not follow octet rule thus it applies mainly to the second period elements of the periodic table.

## Formal Charge on an Atom in a Molecule/Ion

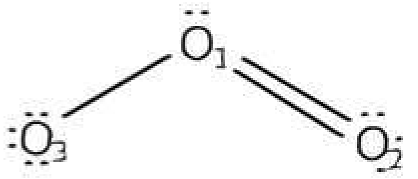
The individual atom in a polyatomic molecule is composed of a charge which is named a formal charge.

Formal Charge (F. C.) = [total number of valence electrons in the free atom]

– [total number of non-bonding (lone pair) electrons]

$-\frac{1}{2}$ [total number of bonding (bond pair) electrons]

Example.

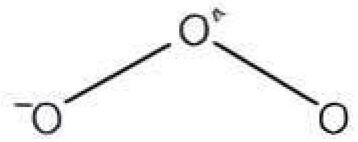


$$\text{F.C on } O_1 = 6 - 2 - \frac{1}{2}(6) = +1$$

$$\text{F.C on } O_2 = 6 - \frac{4}{2} - 4 = 0$$

$$\text{F.C on } O_3 = 6 - 6 - \frac{2}{2} = -1$$

Thus, the formal charges represented in $O_3$ are as follows:



### Important

- When compared to an isolated neutral atom, the formal charge on an atom in a molecule represents the electron count associated with the atom. Knowing the formal charge on a certain atom in a structure is crucial for keeping track of electrons and determining and forecasting reactivity.

## TOPIC 2

# TYPES OF CHEMICAL BOND

There are three types of chemical bond:

(1) Ionic Bond
(2) Covalent Bond
(3) Coordinate Bond

## Ionic or Electrovalent Bond

An ionic bond is formed when electrons are transferred from one atom or molecule to another atom or molecule, resulting in the formation of a chemical connection. The atom or molecule which obtains an electron carries a negative charge (anion) and that atom or molecule which gives an electron carries a positive charge (cation).

The ionic bond becomes stronger when there is a large electronegativity difference between the two atoms. The higher the difference in electronegativity between cation and anion, the stronger is the ionic bond.

### Important

- An ionic bond is an extreme example of a polar covalent bond, with the latter resulting from unequal electron sharing rather than entire electron transfer. When the electronegativities of two atoms differ greatly, ionic bonds occur, whereas covalent bonds form when the electronegativities are identical.

### Explanation of ionic bond

Atoms are generally neutral which means they have an equal number of electrons and protons. So, when they lose or gain electrons, they become positively or negatively charged.

$$X \rightarrow X^{+} + e^{-};\ \text{Ionisation enthalpy}$$

In this case, the atom X loses one electron and thus, attains a positive charge.

$$Y + e^{-} \rightarrow Y^{-};\ \text{Electron gain enthalpy}$$

Furthermore, in the case of an atom Y, it gains one electron so it becomes a negative ion.

When both ions are attracted to each other because of electrostatic forces of attraction, then a new bond is formed and this bond is termed as an ionic bond.

$$X^{+} + Y^{-} \rightarrow XY$$

### Factors affecting the formation of ionic bonds

(1) **Ionisation Enthalpy (Ionisation Energy):** It is the amount of energy required to remove an electron from an isolated gaseous atom. Thus for formation of an ionic bond element should have low ionisation enthalpy.

(2) **Electron Gain Enthalpy (Electron Affinity):** It is the enthalpy change associated with an isolated gaseous atom when it gains an electron to form its corresponding anion. During the addition of an electron, energy can either be released or absorbed. Electron affinity is the negative of the electron gain enthalpy. Thus, for the formation of an ionic bond element should have a high negative value of electron gain enthalpy.

(3) **Lattice Enthalpy (Lattice Energy):** To form ionic compounds, cation and anion combine to form the compound. Measurement of the ionic bond's strength and its stability in the ionic compound is given by lattice energy. It is the energy required to completely separate one mole of a solid ionic compound into gaseous constituent ions. For example, the lattice enthalpy of NaCl is 788 kJ $\text{mol}^{-1}$. This

means that 788 kJ of energy is required to separate one mole of solid NaCl into one mole of $Na^+_{(g)}$ and one mole of $Cl^-_{(g)}$ to an infinite distance. The higher the value of lattice energy, the higher is the ease of formation of ionic compounds.

### General characteristics of ionic compounds

(1) These substances are solids. The ions are structured and brittle because they are held together by strong electrostatic forces.

(2) High melting and boiling temperatures are required to disintegrate the molecules as they may be held together by strong electrostatic forces.

(3) They are soluble in polar solvents like water, but not so much soluble in non-polar solvents like benzene, $CCl_4$ etc.

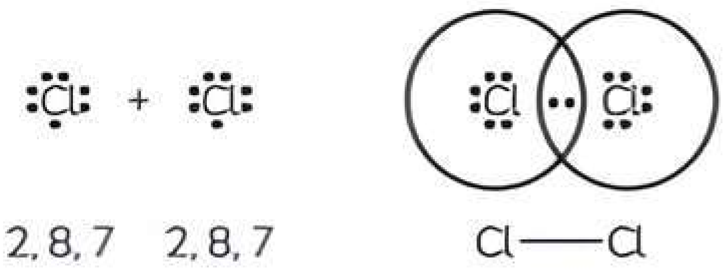
(4) In a molten state and aqueous solution, ionic compounds are the good conductors of electricity. This is because the electrons or ions are free to move but solid ionic compounds are closely packed which doesn't allow any movement of ions thus making them a bad conductor of electricity.

(5) They are crystalline in nature. However, the dimensions of the crystalline structure are determined by the anions and cations' diameters. As to form an ionic compound, several cations should be equal to several anions. The whole ionic compounds are uncharged or neutral.

## Covalent Bond

When there is a mutual sharing of electrons among two atoms to acquire their octets or duplets, a chemical bond is formed between them. These bonds are known as covalent bonds. Each atom donates several electrons termed as covalency.

For example, formation of $Cl_2$:



Bond pairs refer to shared pairs of electrons between two atoms in covalent bonding, whereas lone pairs refer to unshared pairs of electrons between two atoms in covalent bonding.

### Types of covalent bond

(1) **Non-polar covalent bond:** A non-polar covalent bond is a type of chemical bond that is formed when electrons are shared equally between two atoms having almost the same electronegativities. Example, $H_2$, $Cl_2$ etc.

(2) **Polar covalent bond:** A polar covalent bond is a type of chemical bond formed between two atoms in molecules having an electronegative difference. H-Cl, $CO_2$, etc.

### Factors affecting the formation of covalent bonding

(1) Ionisation energy: For formation of covalent bonds, the ionisation energy of atoms should be high.

(2) Electron gain enthalpy: The atoms should have equal electron gain enthalpy for the formation of covalent bonds.

(3) Electronegativity: For formation of covalent bonds, the atoms should have almost equal electronegativities.

### General characteristics of covalent compounds

(1) Covalent compounds exist in a liquid or gaseous form at ambient temperature because of weak intermolecular interactions. However, a diamond is a covalent compound that is solid at room temperature.

(2) They have low melting and boiling points because weak intermolecular bonds require less energy to break, except for diamond, whose melting point is high as it has many covalent bonds so a high temperature is required to break the bonds.

(3) Covalent compounds are often poor conductors because they lack free electrons or ions to carry electricity. However, graphite is a covalent compound that is a good conductor of electricity as carbon atoms are bonded in layers with three strong covalent bonds that gave spare electrons which conduct electricity.

(4) Covalent compound is soluble in a non-polar solvent such as benzene but usually insoluble in water.

**Example 1.4:** Case Based:

*Chemical bonding is the process of atoms joining together to form molecules, ions, crystals, and other stable species that make up the recognisable components of everyday life. When atoms come close together, their nuclei and electrons interact and tend to disperse themselves in space in such a way that the total energy is lower than in any other configuration. When the overall energy of several atoms is lesser than the summation of the energies of the individual atoms, bonding occurs. After the electron was discovered and quantum mechanics gave a system for describing the behaviour of electrons in atoms, the theories that contributed to determining the nature of chemical bonding came to fruition in the early twentieth century. Despite the fact that quantum physics is required to gain full quantitative knowledge of bond formation, chemists' pragmatic understanding of bonding is expressed in simple intuitive models. These models distinguish between two types of bonds: ionic and covalent. The* *sort of bond that is most likely to form between two atoms may be anticipated based on the elements' positions in the periodic table, and the qualities of the substances generated can be linked to the type of bonding to some extent.*

**(A) Which of the following chlorine compounds is composed of both ionic and covalent bonds?**

(a) NaCl (b) $NaClO_4$
(c) $PCl_3$ (d) $POCl_3$

**(B) In $PO_4^{-3}$, the formal charge upon every atom and P — O bond order respectively is:**

(a) –0.75, 1.25 (b) –0.75, 1.0
(c) –0.75, 0.6 (d) –3, 1.25

**(C) Calculate the formal charge on the central oxygen atom in $O_3$ molecule.**

**(D) Which of the following elements has an electrovalent bond?**

**$CaCl_2$; $AlCl_3$; $SiCl_2$; $PCl_3$**

**(E) Asserion (A): Oxygen atoms get an octet of electrons during the formation of the water octet molecule.**

**Reason (R): Oxygen atom forms two ionic or electrovalent bonds with two hydrogen atom.**

**A statement of assertion followed of reason is given. Choose the correct answer out of the following choices:**

**(a) Both (A) and (R) are true and (R) is the correct explanation of (A).**
**(b) Both (A) and (R) are true but (R) is not the correct explanation of (A).**
**(c) (A) is true but (R) is false.**
**(d) (A) is false but (R) is true.**

**Ans. (A)** *(b) $NaClO_4$*

**Explanation:** $NaClO_4$ is made up of two parts: $Na^+$ and $ClO_4^-$ ions with ionic bonding. In $ClO_4^-$ (perchlorate ion) Cl–O bonds, on the other hand, are covalent.

**(B)** *(a) –0.75, 1.25*

**Explanation:** The formal charge on each O-atom in

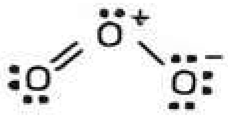
$$PO_4^{3-} = -\frac{3}{4} = -0.75$$

P–O bond order in $PO_4^{3-}$

$$= \frac{\text{Total number of bonds between atoms}}{\text{Total number of resonating structures}}$$

$$= \frac{5}{4} = 1.25$$

**(C)** The structure of $O_3$ is.



$$\text{Formal charge (F.C.)} = V - L - \frac{B}{2}$$

Where.

$V$ = Total number of valence electrons in the atom.

$L$ = Total number of non-bonding (lone pair) electrons in the atom.

$B$ = Total number of bonding (shared) electrons in that particular atom.

Hence, the formal charge on the central O atom in $O_3 = 6 - 2 - \frac{1}{2} \times 6 = +1$

**(D)** Because there is an electronegativity difference between the Ca and Cl atoms in $CaCl_2$, thus Ca–Cl bond are electrovalent or ionic bonds.

**(E)** *(c) (A) is true and (R) is false*

**Expalnation:** In order to fulfill the hydrogen atom's duplet and the oxygen atom's octet, each oxygen atom establishes a covalent bond with a hydrogen atom during the synthesis of the water molecule.

## OBJECTIVE Type Questions

[ 1 mark ]

## Multiple Choice Questions

**1. The formation of the electrovalent bond is easier if the difference in the electronegativity of the two atoms is:**

(a) high (b) low
(c) equal (d) None of these

[Diksha]

**Ans.** *(a) high*

**Explanation:** When electronegativity difference is higher than ion formation takes place hence ionic bond is formed.

**Caution**

➥ *Students should remember that in each bond pair, there are two electrons. For example, let a compound has two bond pairs then there are four electrons.*

**2. The electronic configurations of the element I., II. and III. are given below. Answer the questions on the basis of these configurations.**

I. $1s^2\ 2s^2\ 2p^6$

II. $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$

III. $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$

The bond between II and III will be:

(a) Ionic (b) Covalent
(c) Hydrogen (d) Coordinate

[NCERT Exemplar]

**Ans.** *(b) Covalent*

**Explanation:** As we know bonds formed between two non-metals are mostly covalent. Here B and C are non-metals, so they will form a covalent bond.

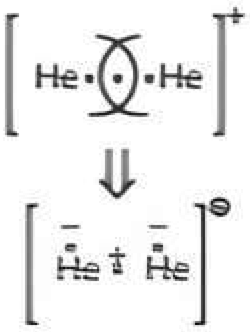
**3. Using Kossel and Lewis's approach, tell which of the following molecules has a complete octet on the central atom.**

(a) $He_2^+$ (b) NO
(c) $ClO_2^-$ (d) $CO_2$

**Ans.** *(d) $CO_2$*

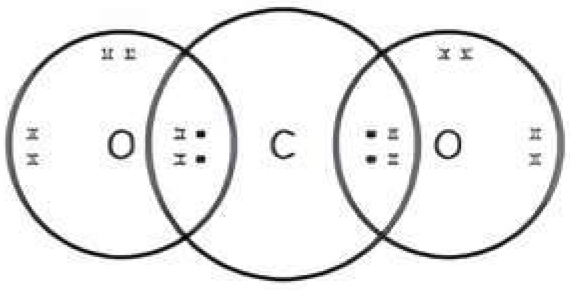
**Explanation:** According to Kossel-Lewis's approach, in the molecule $CO_2$, the central atom has a complete octet whereas

$He_2^+$



NO = $:\overset{-}{\ddot{N}} = \ddot{O}:$ and $ClO_2^-$ have an incomplete octet $:\underset{..}{\ddot{O}}^- — \underset{..}{\ddot{Cl}} = \ddot{O}:$.

Lewis's structure of $CO_2$ is:



**4. Covalent compounds are most simply formed with:**

(a) low electron affinity, high ionisation energy
(b) high electron affinity, low ionisation energy
(c) high electron affinity, high ionisation energy
(d) low electron affinity, low ionisation energy

**Ans.** *(c) high electron affinity, high ionisation energy*

**Explanation:** Covalent compounds are formed when:

(1) When two atoms have a strong and equal electron affinity, then a covalent bond is formed.

(2) Both the atoms which are participating in covalent bond formation should have high ionisation enthalpy.

**5. The electrovalent compound dissolves in a solvent if the value of .................. energy is higher than the .................. energy of the ionic compound.**

(a) lattice, solvation
(b) ionisation, solvation
(c) ionisation, lattice
(d) solvation, lattice [Diksha]

**Ans.** *(d) solvation, lattice*

**Explanation:** The ions of an ionic compound are separated and solvated by the solvent molecules during dissolution. Solvation energy is the energy released when ions are surrounded by solvent molecules, whereas lattice energy is the energy necessary to remove ions from a compound's lattice. The solute is insoluble in a solvent if the lattice energy exceeds the solvation energy and no external energy is given.

**6. Which of the molecules below does not have a dative bond?**

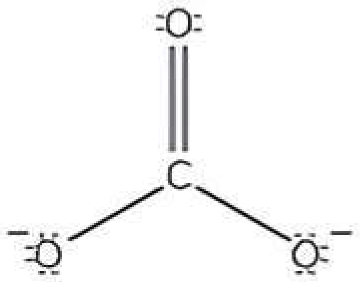
(a) CO (b) $CO_3^{2-}$
(c) $SO_4^{-2}$ (d) All of these

**Ans.** *(b) $CO_3^{2-}$*

**Explanation:**

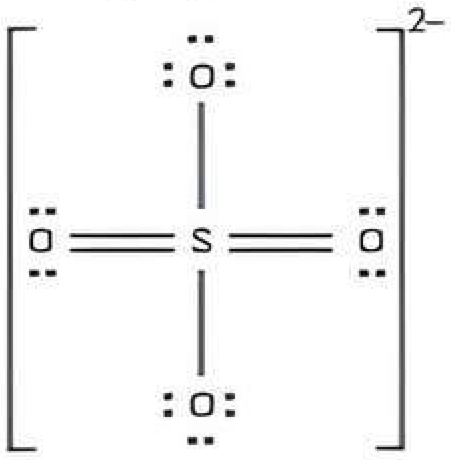
(a) $:C \equiv O:$ Here, oxygen shares its electron with carbon and both C and O have a complete octet. Thus, it is following octet rule and has a dative bond.

(b)



The carbon atom makes one double bond with an oxygen atom and two single bonds with the other two oxygen atoms in the middle. The oxygen atoms, even though they have a lone pair of electrons, will not establish a dative bond with the central C atom because the core C has already acquired a stable configuration.

(c)



Here, sulphur shares its electron and makes a coordinate bond with two oxygen atoms. Then, S and all four O have a complete octet and it has a dative bond.

### Related Theory

- Dative Bond: A coordinate bond (sometimes referred to as a dative covalent connection) is a sort of covalent bond (by sharing pair of electrons) in which both electrons originate from the same element. When two atoms share a pair of electrons, they form a covalent bond. Because both nuclei are attracted to the electron pair, the atoms are stuck together.

## Assertion-Reason (A-R)

In the following question no. (7–9) a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choice.

(a) Both (A) and (R) are true and (R) is the correct explanation of (A).
(b) Both (A) and (R) are true but (R) is not the correct explanation of (A).
(c) (A) is true but (R) is false.
(d) (A) is false but (R) is true.

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

Reason (R): This is because sodium and chloride ions acquire octet in sodium chloride formation. [NCERT Exemplar]

**Ans.** *(a) Both (A) and (R) are true and (R) is the correct explanation of (A).*

**Explanation:** Sodium and chloride ions in NaCl have a complete octet. Therefore, NaCl is a stable compound.

$$Na^+ + Cl^- \rightarrow NaCl^-$$

**8.** Assertion (A): The form of the molecule is not explained by the octet hypothesis.

Reason (R): The octet theory can predict a molecule's relative stability and energy.

**Ans.** *(c) (A) is true but (R) is false.*

**Explanation:** The octet rule does not account for the shape of molecules or explain their relative stability, and it is completely mute concerning a molecule's energy.

**9.** Assertion (A): For the identical halides, the order of lattice energy is LiF > NaF > KF.

Reason (R): From Li to K, the size of alkali metals rises.

**Ans.** *(b) Both (A) and (R) are true but (R) is not the correct explanation of (A).*

**Explanation:** As we know that the size of the cation or anion is inversely proportional with the lattice energy. Since the anion is identical in all cases, the lattice energy is only dependent on the size of the cation. The following is the size order of the specified cations in ascending order:

$$Li^+ < Na^+ < K^+$$

As a result, the order of lattice energy is:

$$LiF > NaF > KF$$

## CASE BASED Questions (CBQs)

[ **4** & **5** marks ]

Read the following passages and answer the questions that follow:

**10.** *Electron dot structures or Lewis dot formulas can be drawn if the molecular formula of the compound is known. It defines the nature of bond and position of atoms of the molecule which are connected in the molecule. The representation of molecules in Lewis electron dot structure or just a Lewis structure is in honour of the American chemist Gilbert Newton Lewis. Lewis dot structures also called electron dot structures are diagrams that describe the chemical bonding between atoms in a molecule. They also display the total number of lone pairs present in each of the atoms that constitute the molecule. Lewis dot structures are commonly referred to as electron dot structures or Lewis structures. Lewis defined a base as an electron pair donor and an acid as an electron pair acceptor. Lewis dot structures reflect the electronic structures of the elements, including how the electrons are paired. Lewis structures are a useful way to summarize certain information about bonding and may be thought of as "electron bookkeeping". In the Lewis dot structure, each dot represents an electron. A pair of dots between chemical symbols for atoms represents a bond.*

(A) Which of the following conditions doesn't apply to Lewis dot structure?

(I) Each bond is created as a result of the atoms sharing an electron pair.

(II) Only one atom from the two combining atoms contributes electron(s) to the shared pair.

(III) The sharing of electrons allows the atoms to achieve the outer shell noble gas structures.

Options:

(a) (I) and (III)
(b) (II) and (III)
(c) Only (II)
(d) Only (III)

(B) The structure with the ............... formal charges on the atoms has the lowest energy.

(a) smallest
(b) highest
(c) zero
(d) negative

(C) Identify the group valence of atoms in the halogen family.

(a) 2
(b) 1
(c) 9
(d) 7

(D) Which rule is followed by sharing or transfer of electrons from one atom to the other to attain a stable octet configuration?

(a) Duet rule
(b) Triplet rule
(c) Octet rule
(d) Septet rule

(E) For which molecule octet rule is not valid?

(a) $H_2O$
(b) CO
(c) $CO_2$
(d) $O_2$

**Ans.** (A) *(c) (II) only*

**Explanation:** To form covalent bonds we need two atoms at least so that sharing of electrons can take place. Thus, (II) is not appropriate for the Lewis structure.

(B) *(a) smallest*

**Explanation:** The structure with the least formal charge on the atoms has the lowest energy.

(C) *(b) 1*

**Explanation:** The group valence can be calculated from Lewis symbols either by subtracting it from eight (more than 4) or having it equal (less than 4). The halogen family has 7 electrons in their outer orbit. So 8 – 7 = 1. Therefore, the valency of the halogen family is 1.

(D) *(c) Octet rule*

**Explanation:** As per the electronic theory of chemical bond that's put forth by Lewis and Kossel states that the atoms follow the octet rule by sharing or transfer of electrons from one atom to the other to attain a stable octet configuration.

(E) *(b) CO*

**Explanation:** In CO molecule, the carbon atom contains only six valence electrons whereas eight electrons are required to fulfill its octet.

Hence, CO molecule does not have an octet. The Octet rule is not valid for CO molecule.

**11.** *Lattice energy is a measure of the strength of the ionic bonds in an ionic compound. It provides insight into several properties of ionic solids including their volatility, their solubility, and their hardness. The lattice energy of an ionic solid cannot be measured directly. However, it can be estimated with the help of the Born-Haber cycle. Generally, this quantity is expressed in terms of kilojoules per mole (kJ/mol). Lattice energy can be defined as the energy required to convert one mole of an ionic solid into gaseous ionic constituents. Alternately, it can be defined as the energy that must be supplied to one mole of an ionic crystal in order to separate it into gaseous ions in a vacuum via an endothermic process. Therefore, this quantity always holds a positive value. Some sources define lattice energy in the opposite manner, i.e. the amount of energy released when an ionic solid is formed from its gaseous ionic constituents via an exothermic process. According to this definition, lattice energy must always hold a negative value due to the electrostatic forces between them, the individual ions in an ionic lattice are attracted to each other. The strength of the electrostatic force of attraction is directly proportional to the magnitude of the charge held by the constituent ions, i.e. the greater the charge, the stronger the force of attraction and the stronger the lattice. For example, the lattice energy of calcium chloride is greater than that of potassium chloride despite the similarity in the crystal arrangements of these compounds. This is because the magnitude of the positive charge held by the calcium cation (+2) is greater than that held by the potassium cation (+1). As a consequence of this, the electrostatic forces of attraction are stronger in calcium chloride (than those in potassium chloride). Therefore, the lattice energy of $CaCl_2$ is greater than that of KCL.*

**(A)** $AlCl_3$ has a higher lattice enthalpy than $MgCl_2$. Explain.

**(B)** List the lattice energies of lithium halides in decreasing order.

**(C)** Which of the two salts, NaCl or CsCl, has the higher lattice energy and why?

**Ans.** (A) As charge is higher and size is smaller of $Al^{3+}$. Charge is directly proportional and size is inversely proportional to lattice energy. Hence, $AlCl_3$ has higher lattice enthalpy than $MgCl_2$.

(B) LiI < LiBr < LiCl < LiF

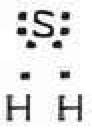
(C) Lattice energy is proportional to ion charge and inversely proportional to atom radius. Now, between NaCl and CsCl, the radius of $Cs^+$ is far greater than that of $Na^+$; even though CsCl is more ionic, the radius is greater, and thus, the lattice energy is lower.

## VERY SHORT ANSWER Type Questions (VSA)

[ 1 mark ]

**12. Draw the Lewis dot structure of $H_2S$ molecule.**

**Ans.** Lewis's dot structure of $H_2S$ molecule:



**13. Define the term "electrovalency."**

**Ans.** The number of electrons given or received by an element's valence shell to achieve a stable electronic configuration is referred to as electrovalency.

**14. What do bond pair electrons and lone pair electrons mean to you?**

**Ans.** Those electron pairs of covalent compounds that take part in bond creation are called bond pair electrons while those which do not take part in bond creation are called lone pair electrons.

## SHORT ANSWER Type-I Questions (SA-I)

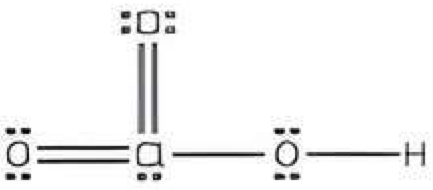
[ 2 marks ]

**15. The ionic bonds have a partial covalent character. Why?**

**Ans.** As we all know that no ionic bond is 100% ionic. It has some covalent character. Suppose we take two atoms A and B. $A^+$ attract $B^-$ but it repels the nucleus which creates some distortion. Electron clouds around distorted valence electrons get shared which is covalency.

**16. In $HClO_3$, compute the chlorine's formal charge.**

**Ans.** By using Lewis's structure, we can determine the formal charge on Cl



Bonded electrons = 10

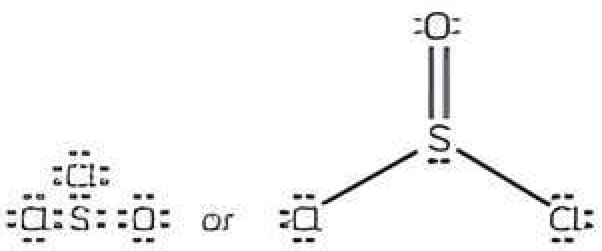
$$\text{Formal charge} = 7 - 2 - \frac{1}{2}(10)$$
$$= 7 - 2 - 5$$
$$= 0$$

**17. What do bond pair electrons and lone pair electrons mean to you?**

**Ans.** Those electron pairs of covalent compounds that take part in bond creation are called bond pair electrons while those which do not take part in bond creation are called lone pair electrons.

**18. Draw the Lewis structure of thionyl chloride.**

**Ans.** Lewis structure of thionyl chloride ($SOCl_2$) is:



## SHORT ANSWER Type-II Questions (SA-II)

[ 3 marks ]

**19.** Explain the difference between an ionic and a covalent bond.

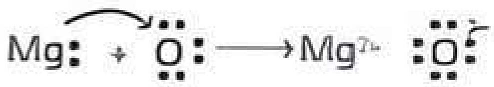
**Ans.**

| S. No. | Ionic bonds | Covalent bonds |
|---|---|---|
| (1) | In ionic bonds, one atom donates an electron and the other atom accepts that electron making the whole molecule stable. | The atoms in a covalent bond are held together by the sharing of electrons, resulting in the formation of a covalent molecule. |
| (2) | The electro-negativity of various elements varies. | The bond is called nonpolar when the electron is shared coordinately amongst the atoms creating a covalent bond. |
| (3) | The formation of a polar bond happens because of the attraction of oppositely charged ions. | The creation of a polar covalent bond occurs when an electron is more attracted to one atom than to another. |

**20.** What is an ionic bond? Explain with two suitable examples. [NCERT Exemplar]

**Ans.** When there is the complete transfer of electrons among two atoms resulting in positive and negative charge and then a bond is formed between them is known as an ionic bond. For example, NaCl

$Mg^{2+} + O^{2-} \longrightarrow Mg^{2+}\ O^{2-}$ or MgO



Or MgO

**21.** Is it $MgF_2$ or $MgCl_2$ that is more soluble? Justify your response.

**Ans.** $MgCl_2$. Because the hydration/solvation energy of $MgCl_2$ is higher than the lattice energy, it is highly soluble, but the lattice energy of $MgF_2$ is significantly higher than the hydration energy [because $F^-$ is a tiny ion and the forces of attraction between the molecules are high]. As a result, it is less soluble.

## LONG ANSWER Type Questions (LA)

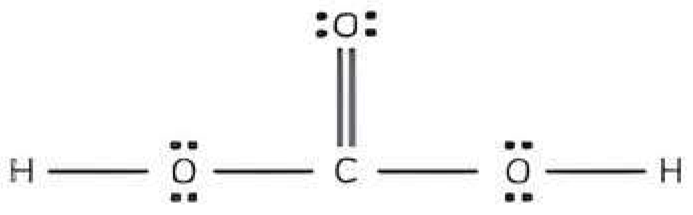
[ 4 & 5 marks ]

**22.** Make Lewis's structure of the given compounds.

(A) $H_2CO_3$ (B) $SF_6$
(C) $PF_5$ (D) $IF_7$
(E) $CS_2$

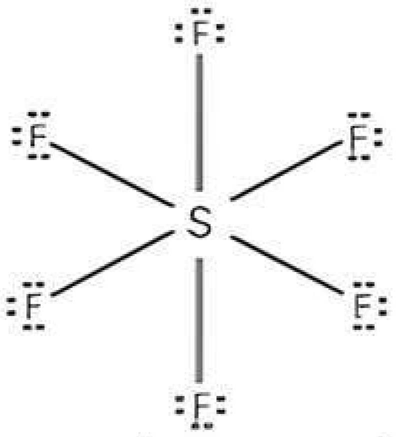
In these circumstances, is the octet rule followed?

**Ans.** (A)



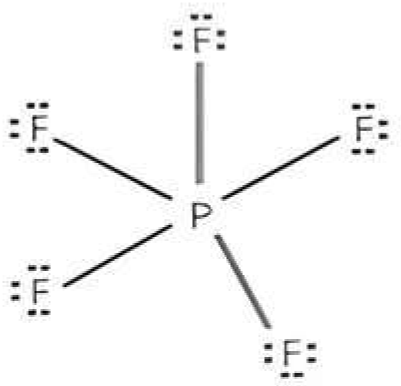
All atoms are accepting octet rule.

(B)



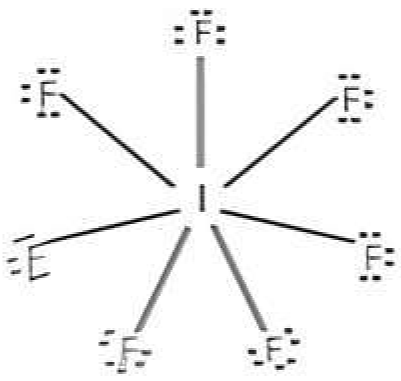
Here, S atom has more than eight electrons. Thus, do not obey the octet rule.

(C)



Here, P is an expanded octet which means there are more than eight electrons. So, it does not follow the octet rule.

(D)



Here, I does not follow the octet rule.

(E) 

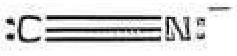
Here, carbon atoms have two double bonds and C and S both also obey the octet rule.

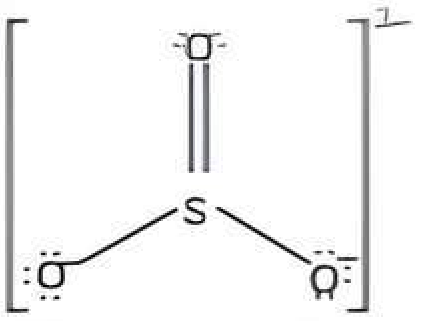
**23.** Create electron dot structures for the following:

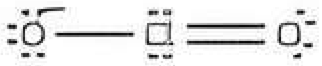
(A) $CN^-$

(B) $SO_3^{2-}$

(C) $ClO_3^-$

**Ans.** (A) 

(B) 

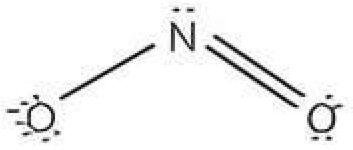
(C) 

**24. What is the meaning of a formal charge? In the nitrite ion, write the formal charges of the atoms.**

**Ans.** The individual atom in a polyatomic molecule is composed of a charge which is named a formal charge. In the other words, the charge assigned to an atom present in a molecule is referred to as a formal charge (F.C or q), assuming that regardless of relative electronegativity, electrons in all chemical bonds are evenly shared among atoms.

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

Here, $V$ is the number of valence electrons in free atoms, $L$ is the lone pairs electron and $S$ is the bond pair electron. So, in nitrite ion,



For N,

$$= 5 - 2 - \frac{1}{2} \times 6$$

$$= 3 - 3$$

$$= 0$$

For O,

$$= 6 - 4 - \frac{1}{2} \times 4$$

$$= 2 - 2$$

$$= 0$$

For $O^-$,

$$= 6 - 6 - \frac{1}{2} \times 2$$

$$= -1$$

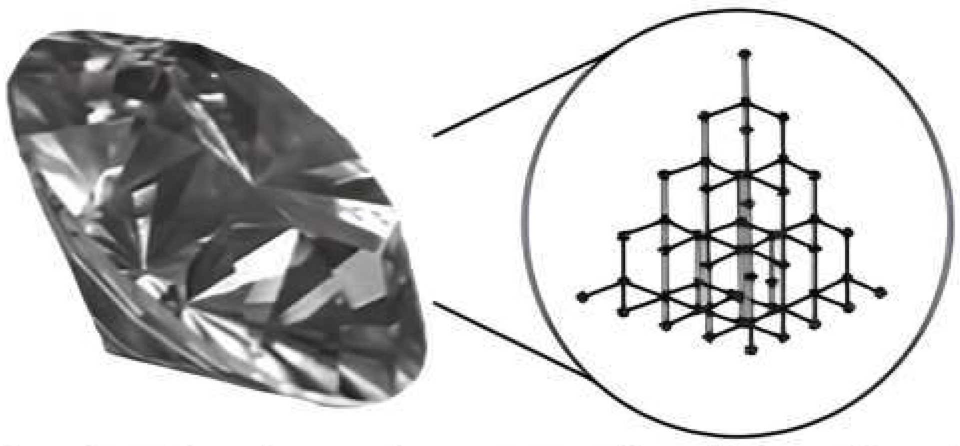
Therefore, the total charge is −1.

◆

# BOND PARAMETERS

2

We all know a diamond is an attractive object. For centuries, people have adored the brilliance of these gems. While it is a perfect object to express their affection to someone, others consider it the most valuable commodity to acquire. Diamond is also used industrially for cutting, grinding, sawing, and drawing wire. The hardness of a diamond can be understood by its crystal structure. Each carbon atom is attached to four other carbon atoms via covalent bonding in a regular tetrahedral structure and by this continous bonding, they form a giant structure. This covalent bonding includes different factors through which each of the molecules is bonded. And these factors are called bond parameters.



Covalent bonds are characterised by different bond parameters. These bond parameters offer a vision of the stability of a chemical compound and the strength of the chemical bonds holding its atoms together. There are six bond parameters through which bonds can be characterised. They are:

(1) Bond length

(2) Bond angle

(3) Bond energy/ enthalpy

(4) Bond order

(5) Resonance

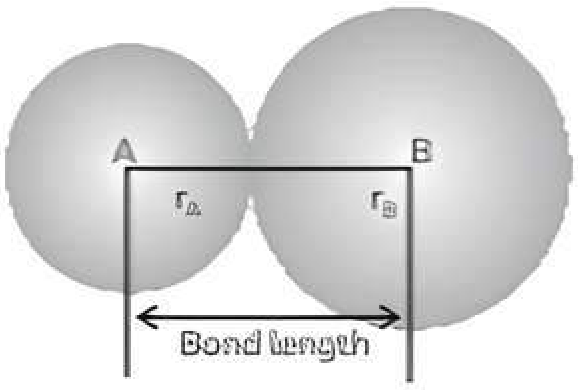
(6) Polarity of bonds

## Bond Length

The bond length of a molecule refers to the equilibrium distance between the nuclei of two bonded atoms. Angstrom or picometer units are used to measure bond lengths. X-ray diffraction of solids and electron diffraction of gases techniques are used to determine it spectroscopically. Two bonded pairs are added together to generate bond lengths.

(1) In ionic compounds, the bond length may be estimated by adding the radii of the cations and anions, i.e., $r_{C+} + r_{A-}$ and the link formed between the ions is known as an ionic bond.

(2) The bond length of covalent compounds is computed by summing the radii of two bonded atoms, i.e., $r_A + r_B$ and the bond created between the atoms is referred to as a covalent bond. The covalent radius is the distance between two identical atoms in the same molecule divided by two, i.e., $\frac{r_A + r_B}{2}$.



(3) In a solid state, the van der Waals radius is half the distance between two identical atoms of different molecules. It represents the overall size of the atom which includes its valence shell in a non-bonded situation.

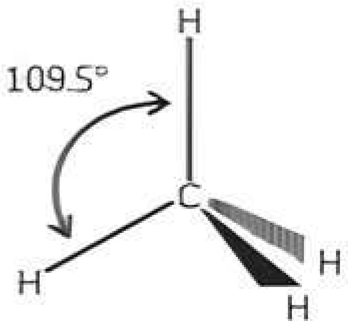
**Table: Average Bond lengths for Some Single, Double and Triple Bonds**

| Bond | Bond Length (Å) | Bond | Bond Length (Å) |
|---|---|---|---|
| C—C | 1.54 | N—N | 1.47 |
| C=C | 1.34 | N=N | 1.24 |
| C≡C | 1.20 | N≡N | 1.10 |
| C—N | 1.43 | N—O | 1.36 |
| C=N | 1.38 | N=O | 1.22 |
| C≡N | 1.16 | O—O | 1.48 |
| C—O | 1.43 | O=O | 1.21 |
| C=O | 1.23 | | |
| C≡O | 1.13 | | |

## Bond Angle

A bond angle is an angle made by two or more atoms between two adjacent bonds. It helps in the determination of the shape of a particular molecule. The bond angles are expressed in a degree which is determined experimentally. Also, it is used for determining the lone pairs of electrons of an atom. The more the number of lone pairs, the less is the bond angle due to the repulsion.

**Example:** Bond angle between C–H in $CH_4$ is depicted in the following figure:



## Bond Enthalpy

The amount of energy required to break one mole of bonds between two atoms in a gaseous state is called bond energy or bond enthalpy.

It is expressed in $kJ\ mol^{-1}$.

**Example:** Cl–Cl bond enthalpy in chlorine molecule is 242 $kJ\ mol^{-1}$.

$Cl_{2(g)} \rightarrow Cl_{(g)} + Cl_{(g)}$ ; $\Delta H = 242\ kJ\ mol^{-1}$.

$O_2$ (O = O) bond enthalpy in oxygen molecule is 497kJ $mol^{-1}$.

$O_2(O = O)_{(g)} \rightarrow O_{(g)} + O_{(g)}$ ; $\Delta H = 497\ kJ\ mol^{-1}$.

**Important**

➥ *The higher is the bond dissociation enthalpy, the stronger will be the bond of the molecule.*

The average bond enthalpy is determined for bond strength calculations in polyatomic molecules like $H_2O$, $CH_4$, $C_2H_5OH$, etc. The bond dissociation enthalpy is divided by the number of bonds broken to get the average bond enthalpy.

Example:

$CH_{4(g)} \rightarrow 4H_{(g)} + C_{(g)}$ ; $\Delta H = 1640\ kJ\ mol^{-1}$.

$$\text{The average bond energy of the C—H bond} = \frac{1640}{4} = 410\ kJ\ mol^{-1}.$$

| Bond | Bond length (Å) | Bond (dissociation) energy ($kJ\ mol^{-1}$) |
|---|---|---|
| H — H | 0.74 | 436 |
| F — F | 1.44 | 159 |
| Cl — Cl | 1.99 | 243 |
| Br — Br | 2.28 | 193 |
| I — I | 2.68 | 151 |
| H — F | 0.918 | 570 |
| H — Cl | 1.27 | 432 |
| H — Br | 1.42 | 366 |
| H — I | 1.61 | 298 |
| H — O (of $H_2O$) | 0.96 | 460 |
| H — N (of $NH_3$) | 1.01 | 390 |
| H — C (of $CH_3$) | 1.10 | 410 |

## Bond Order

The number of shared pairs of electrons between two atoms in a molecule is referred to as bond order.

Example:

$$O{=}O \quad \text{or} \quad O::O$$

Bond Order = 2 (two shared pairs of electrons)

$$N{\equiv}N \quad \text{or} \quad N{:}{:}{:}N$$

Bond Order = 3 (Three shared pairs of electrons)

Isoelectronic molecules have identical bond order.

Example: $O_2^{2-}$ and $F_2$ have 18 electrons and bond order 1.

$N_2$, $NO^+$ and CO have 14 electrons and bond order 3.

**Important**

➥ *Relation between bond order, bond enthalpy and bond length:*

$$\textit{Bond order} \propto \textit{Bond enthalpy} \propto \frac{1}{\textit{Bond length}}$$

**Example 2.1:** **How do you express the bond strength in terms of bond order? [NCERT]**

**Ans.** As the bond order increases the bond strength increases and the bond length decreases.

$$\text{Bond Order} \propto \text{Bond Enthalpy} \propto \frac{1}{\text{Bond length}}$$

## Resonance

It is found that the properties of certain compounds do not satisfy the Lewis structure. The molecule is then supposed to have several structures. In such a case, resonance is introduced. Resonance is a concept in which two or more alternate valence bond structures are written for a molecule and the actual structure is called the resonance hybrid while the different individual structures are called resonance structures or canonical forms.

Resonance is represented by a double-headed arrow. Also, resonance stabilises the molecule as the energy of resonance hybrid is less than the energy of any single canonical structure.

*Ozone Hybird*

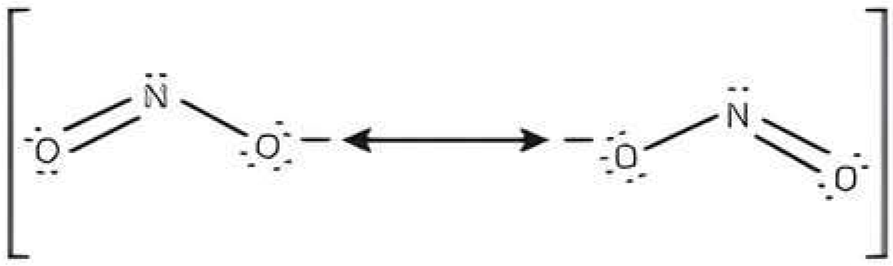
*Ozone Resonating Structures*

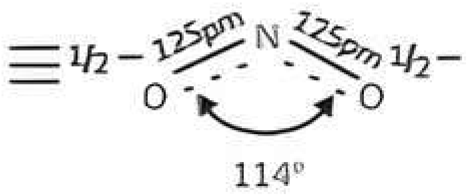
The bond length of O=O is 148pm O=O is 121pm. All O=O bond lengths in $O_3$ are equal and has a value of

128 pm. Hence it is an intermediate between single and double bonds.

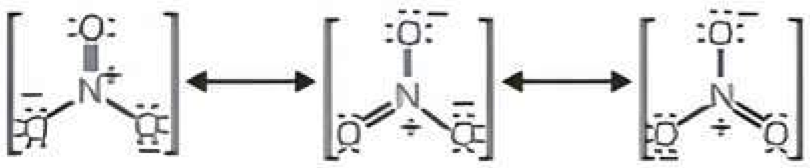
Some other examples of resonating structures can be seen in: $NO_2^-$, $CO_3^{-2}$, $NO_3^-$, etc.

(1) Resonating structure of nitrite ion, $NO_2^-$



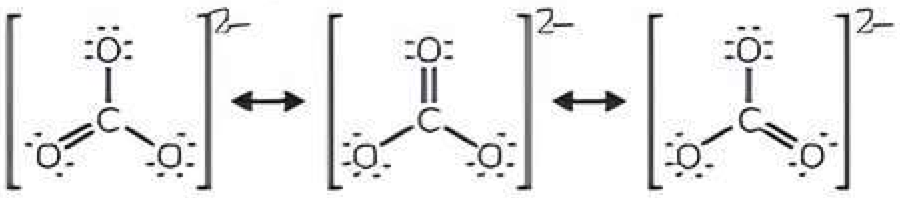


(2) Resonating structure of nitrate ion, $NO_3^-$



**Example 2.2:** Explain the structure of $CO_3^{-2}$ ion in terms of resonance. [NCERT]

**Ans.** According to the Lewis structure, two single bonds and one double between carbon and oxygen atom is insufficient to represent the molecule accurately due to the presence of unequal bonds. Experimental findings prove that all the bonds are equal. So, that's why the carbonate ion is best described in the resonance hybrid form.



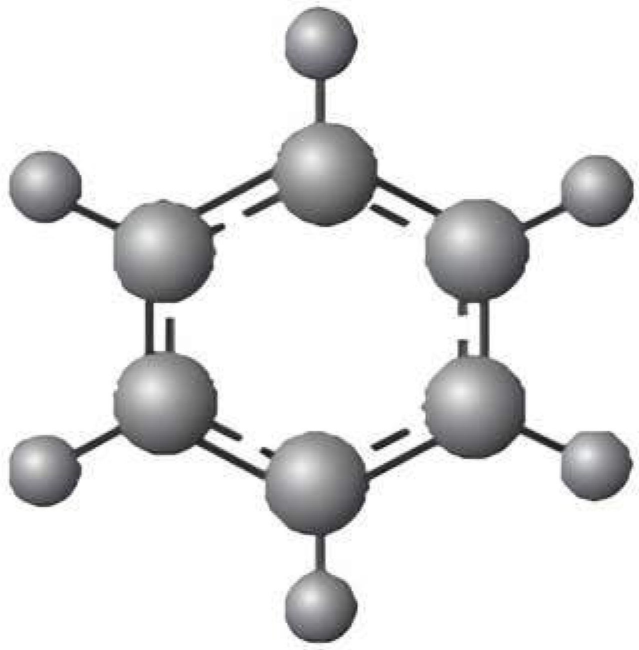
**Example 2.3:** Explain the structure of $CO_2$ molecule. [NCERT]

**Ans.** The bond length between carbon and oxygen in $CO_2$ is 115pm experimentally. The normal C≡O and C=O bond lengths are 110pm and 121pm the carbon-oxygen bond length lies between these two values. Hence, to describe the structures, the resonance structures are formed and the resonance hybrid of canonical structure is the best to describe it.

$$\ddot{O}=C=\ddot{O} \longleftrightarrow :\overset{+}{O}\equiv C-\overset{-}{\ddot{O}}: \longleftrightarrow \overset{-}{\ddot{O}}-C\equiv\overset{+}{O}:$$

**Example 2.4:** Case Based:

*The concept of resonance first appeared in 1899 in Johannes Thiele's "Partial Valence Hypothesis" to explain the unusual stability of benzene which would not be expected from August Kekulé's structure proposed in 1865 with an alternating single. Resonance is an extension of the idea that a Lewis structure can characterise the bonding in a chemical species. A single Lewis structure, consisting of atoms obeying the octet rule, possibly bearing formal charges, and connected by bonds of positive integer order, is sufficient for describing chemical bonding and justifying experimentally determined molecular properties such as bond lengths, angles, and dipole moments for many chemical species. In some cases, more than one Lewis structure can be drawn, and experimental properties contradict any one structure. In order to deal with this kind of circumstance, various contributing structures are averaged out, and the molecule is said to be represented by a resonance hybrid, which combines several Lewis structures to describe its true structure.*



*Benzene resonance Hybrid*

(A) Ozone is a/an ................ molecule and the two O—O bond lengths in ozone are ................ and .................... .

(a) linear, 118pm and 148pm

(b) angular, 110pm and 148pm

(c) linear, 128pm and 148pm

(d) angular, 128pm and 128pm

(B) What type of bond is normally expected between highly electropositive and highly electronegative atoms?

(a) Covalent bond

(b) Ionic bond

(c) Ionic with covalent character

(d) Co-ordinate bond

(C) A bond order of 3 is computed for the diatomic molecule. It is possible that in absence of further information, this triple may be made up of two sigma bonds and one pi-bond. Explain.

(D) Draw the resonating structure of $CO_2$.

(E) Assertion (A): The benzene molecule is stable in spite of the fact that it consists of three double bonds.

Reason (R): Resonance exists in benzene molecules.

(a) Both (A) and (R) are true and (R) is the correct explanation of (A).

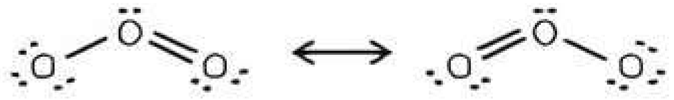
(b) **Both (A) and (R) are true but (R) is not the correct explanation of (A).**

(c) **(A) is true but (R) is false.**

(d) **(A) is false but (R) is true.**

**Ans. (A)** *(d) angular, 128pm and 128pm*

**Explanation:** The O—O bond is present in the resonance hybrid structure. All the O—O have a bond length of 128pm in $O_3$ molecule. It is an intermediate bond length between O—O and O = O.



**(B)** *(b) Ionic bond*

**Explanation:** Ionic bond is present between highly electropositive and highly electronegative atoms. Due to the difference in electronegativity, one tends to lose electrons (high electropositivity) and the other tends to gain electrons (high electronegativity).

**(C)** It is not possible that the triple bond may be made up of two sigma and one pi-bond. The order of filling orbitals and the differentiations existing among the bonding and non-bonding electrons never permit the establishment of more than one sigma bond.

**(D)**

**(E)** *(a) Both (A) and (R) are true and (R) is the correct explanation of (A).*

**Explanation:** The benzene molecule is stable in spite of the fact that it consists of three double bonds this is due to the presence of resonance in the benzene molecule. The C—C bonds (resonance hybrid) in the benzene are 140pm long which is in between single bonds and double bonds.

## Polarity of Bonds (Ionic Nature in Covalent Bond)

Have you ever shared your chocolates with anyone? Chocolates are everyone's favourite and no one wants to share that. When you divide the chocolate, you always want to have the bigger piece. Here someone gets small pieces and some have the bigger pieces. In chemistry, this type of unequal sharing is the basis of bond polarity or dipole.

A homo-diatomic covalent bond is always non-polar while that of a heteroatomic covalent bond is polar. The polarity of any polar covalent bond is determined by the dipole moment. Pauling created the idea of the dipole moment to measure the extent of polarity. The product of magnitude of charges and the distance between the centre of negative and positive charges are known as dipole moment.

Mathematically it is expressed as: $\mu = q \times d$

Here $\mu$ is the dipole moment
$q$ is the magnitude of the charge
$d$ is the separation distance

Dipole moment is expressed in Debye (D).

$$1D = 3.33564 \times 10^{-30} Cm$$

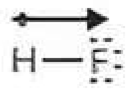
Where, C is coulomb and m is metre.

Or $1D = 1 \times 10^{-18}$ esu-cm

Where, esu is an electrostatic unit.

Dipole moment is a vector quantity. So, it has both magnitude and direction. In chemistry, the presence of a dipole moment is depicted by a crossed arrow placed on the Lewis structure of the molecule, pointing towards the more electronegative atom.

For example: Representation of dipole in HF:



## Dipole Moments of Some Molecular Structures

(1) In a diatomic molecule, $\mu$ depends on the electronegativity difference of atoms i.e., the more the electronegativity difference, the more is the dipole moment ($\mu \propto$ EN).

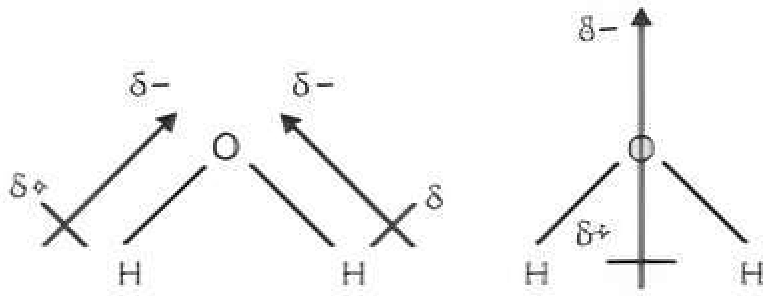
Example: order of $\mu$ : H—F > H—Cl > H—Br > H—I

(2) In a polyatomic molecule, $\mu$ depends on the vector sum of dipole moments of all covalent bonds.

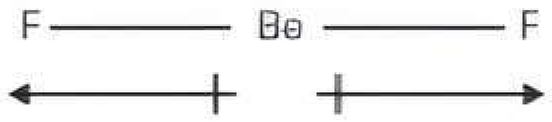
For example: $SiCl_4$, $CH_4$, $CO_2$, $PCl_5$ etc. in these compounds the bond is polar but the compound is nonpolar.

(i) In case of $H_2O$ molecule dipole moment is 1.85D (Debye) or $1.85 \times 3.33564 \times 10^{-30}$ Cm $= 6.17 \times 10^{-30}$ Cm.

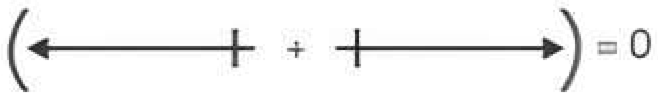
It is the result of dipole moments of two O—H bonds. The dipole moment depends upon the spatial arrangement of the bonds in the molecule.



(ii) In the case of $BeF_2$, the dipole moment is zero because the two equivalent bond dipoles point in opposite directions and cancel the effect of each other.

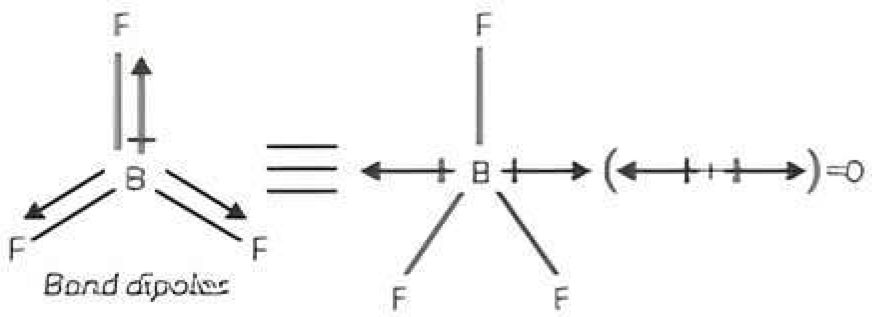


*Bonds Dipoles in $BeF_2$*

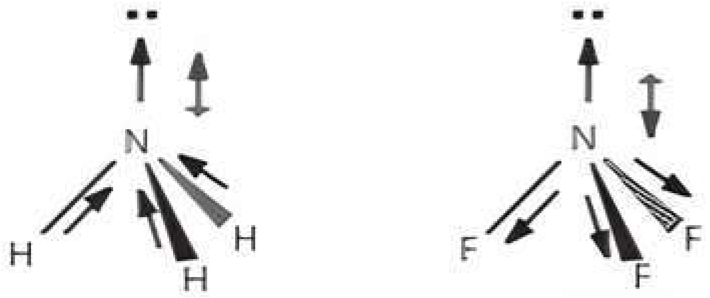


*Total Bond Moment in $BeF_2$*

(iii) In the case of $BF_3$, the dipole moment is zero because the bonds are aligned at an angle of 120° according to the trigonal planar geometry and it is a symmetrical molecule. Hence, the individual dipole moment of polar bonds gets cancelled and the resultant dipole is zero.



(iv) Both $NF_3$ and $NH_3$ have a pyramidal shape with a lone pair of electrons. The electronegativity difference between N and F is greater than that of N and H in $NF_3$ and $NH_3$, the dipole moments are 0.2D and 1.5D respectively because in $NH_3$ the atomic dipole and bond dipole are in the same direction whereas in $NF_3$ these are in opposite directions and thus cancel the resultant dipole moment.



$\mu = 1.46$ D

$\mu = 0.24$ D

**Table: The dipole moment of different types of molecules with their geometry**

| Type of Molecule | Example | Dipole Moment, μ (D) | Geometry |
|---|---|---|---|
| Molecule (AB) | HF | 1.78 | linear |
| | HCl | 1.07 | linear |
| | HBr | 0.76 | linear |
| | HI | 0.38 | linear |
| | $H_2$ | 0 | linear |
| Molecule ($AB_2$) | $H_2O$ | 1.85 | bent |
| | $H_2S$ | 0.95 | bent |
| | $CO_2$ | 0 | linear |
| Molecule ($AB_3$) | $NH_3$ | 1.47 | trigonal-pyramidal |
| | $NF_3$ | 0.23 | trigonal-pyramidal |
| | $BF_3$ | 0 | trigonal-planar |
| Molecule ($AB_4$) | $CH_4$ | 0 | tetrahedral |
| | $CHCl_3$ | 1.04 | tetrahedral |
| | $CCl_4$ | 0 | tetrahedral |

**Applications of dipole moment**

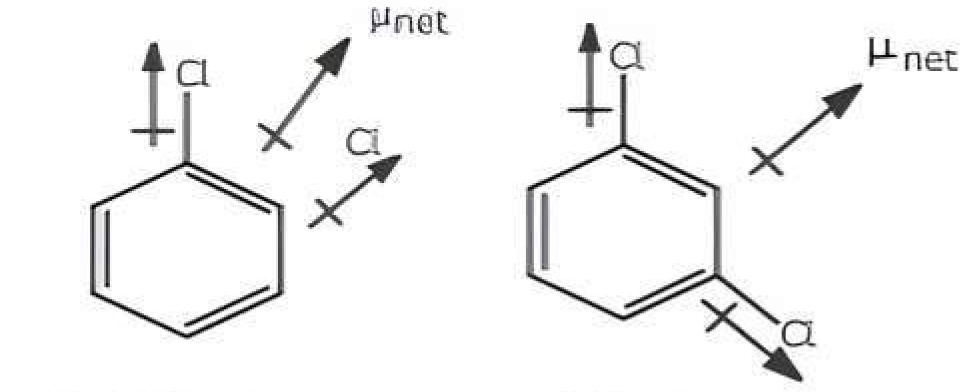
(1) Molecules having zero dipole moment are said to be non-polar molecules while those with $\mu \neq 0$ are called polar molecules.

(2) Dipole moment of *cis*- alkene is more than the dipole moment of *trans*- alkene. Trans alkene has zero dipole due to the presence of symmetry.

(3) Dipole moment ∝ number of lone pairs of electrons. For example: $HF > H_2O > NH_3$. Fluorine has 3 lone pairs, oxygen has 2 lone pairs and nitrogen has one lone pair.

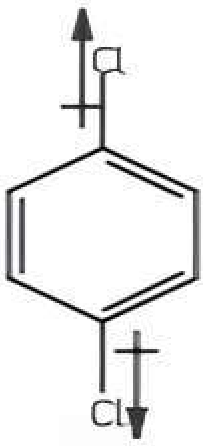
$$\text{Dipole moment} \propto \frac{1}{\theta}$$

For example: *Ortho* > *meta* > *para* benzene



*ortho* dichlorobenzene
$\mu = 2.30$ D

*meta* dichlorobenzene
$\mu = 1.48$ D



*para* dichlorobenzene
$\mu = 0$ D

## Fajan's rule (Covalent character of ionic bond)

No bond is 100% covalent or ionic in nature. It contains partial covalent as well as ionic character. The partial covalent character of ionic bonds was discussed by Fajans. Followings are the rules given by him which are known as Fajan's rule.

(1) The smaller the size of the cation, the larger is the polarisation(distortion) of the anion. Hence, more is the covalent character. For example: LiCl is more covalent than NaCl and KCl because $Li^+$ have a smaller size of cation as compared to that of $Na^+$ and $K^+$.

(2) The larger the size of the anion, the more is the polarisability (the ability of an anion to get polarised by the effect of the cation) i.e., as the size of the anion increases for the given cation, the more is the covalent character. For example:

in the case of halides of calcium, the covalent character increases from $F^-$ anion to $I^-$ anion.

(3) The greater the charge on the cation, the more is the tendency to polarise the anion. Hence more is the covalent character.

(4) If the cation has the same charge and size, then the one with 18 electrons in the outermost shell brings greater polarisability of anion than those with noble gas configuration.

For example: CuCl is more covalent than NaCl.

$Cu^+$ = 2, 8, 18 More covalent and less ionic in nature.

$Na^+$ = 2, 8 More ionic and less covalent in nature.

**Important**

➥ *Overall, it is to be remembered that covalent character is favoured by:*

*(1) Small size of cation*
*(2) The large size of anion*
*(3) A high charge of cation and anion*
*(4) The cation with 18 electrons in the shell*

**Example 2.5:** **Case Based:**

*Following are the parameters related to a bond:*

*(1) Bond length is defined as the equilibrium distance between the nuclei of two bonded atoms in a molecule. Bond length increases with increases is the size of bonded atoms and decreases with an increase in the number of bonds between bonded atoms.*

*(2) Bond angle: In a covalently bonded molecule having more than two atoms, the bonds form an angle with each other, which is known as bond angle. The factors which affect the bond angle are:*

*(a) Lone pair repulsion*
*(b) Hybridisation of central room.*

*(3) Bond enthalpy: It is defined as the amount of energy required to break one mole of bonds of a particular type to separate them into gaseous atoms. It is also known as bond dissociation energy. The greater the bond enthalpy, the stronger is the bond.*

*(4) Bond Order: According to Lewis, in a covalent bond, the bond order is given by the number of bonds between two atoms in a molecule. With the increase in bond order, bond enthalpy increases and bond length decreases.*

**(A)** **Which of the following has a net dipole moment zero?**

(a) $H_2O$ (b) HF
(c) $CHCl_3$ (d) $BF_3$

**(B)** **The molecule having the smallest bond angle is:**

(a) $AsCl_3$ (b) $SbCl_3$
(c) $NCl_3$ (d) $PCl_3$

**(C)** **Among $F_2$ and $Cl_2$ molecules the bond dissociation energy of $Cl_2$ is more than $F_2$. Why?**

**(D)** **Why does the deviation occur from the idealised shape of $NH_3$ molecule?**

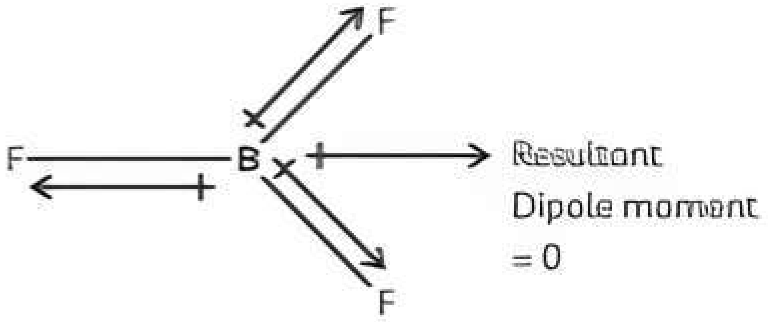
**(E)** **Assertion (A): Water is one of the best solvents.**

**Reason (R): H-bonding is present in water molecules.**

(a) Both (A) and (R) are true and (R) is the correct explanation of (A).
(b) Both (A) and (R) are true but (R) is not the correct explanation of (A).
(c) (A) is true but (R) is false.
(d) (A) is false but (R) is true.

**Ans.** **(A)** *(d) $BF_3$*

**Explanation:** The net dipole moment of $BF_3$ is zero because all the B-F bonds in $BF_3$ are arranged at an angle of 120° to one another. The net result of the three B-F bonds comes to be zero as the resultant of two B-F is equal and opposite to the third one. The structure of $BF_3$ molecule is:



**(B)** *(b) $SbCl_3$*

**Explanation:** The molecule having the smallest bond angle is $SbCl_3$. As we move down the group the size of the central atom increases and the lone pair-bond pair repulsion also increases. Thus, the bond angle decreases. The increasing order of atomic radius is: N < P < As < Sb.

Decreasing order of bond angle is: $NCl_3 > PCl_3 > AsCl_3 > SbCl_3$

**(C)** Among $F_2$ and $Cl_2$ molecules the bond dissociation energy of $Cl_2$ is more than $F_2$. Both the $F_2$ and $Cl_2$ possess three non-bonded electron pairs each. Since fluorine has a small size so, there is larger repulsion between non-bonded electrons in comparison to chlorine. Thus, $Cl_2$ has more bond dissociation energy than $F_2$.

**(D)** Due to the repulsion between bonds, deviation occurs in the $NH_3$ molecule from its idealised shape, and alternations are seen in bond angles of the molecules. The presence of lone pair of electrons causes repulsion between the lone pair-bond pair. Hence, one lone pair of nitrogen repel three bond pairs of N–H.

**(E)** *(b) Both (A) and (R) are true but (R) is not the correct explanation of (A).*

**Explanation:** Water is considered as the best inorganic solvent because of its high dielectric constant value.

Due to the high value of dielectric constant, the electrostatic force of attraction between the ions decreases and these ions get separated and solvated by the solvent molecules.

# OBJECTIVE Type Questions

[ 1 mark ]

## Multiple Choice Questions

**1. The bond length of multiple (double or triple) bonds is always .............. than the corresponding single bond.**

**(a) shorter** **(c) longer**

**(b) equal to** **(d) none of these**

**[Diksha]**

**Ans.** *(a) shorter*

**Explanation:** Multiple bonds are stronger than a single bond. So, the stronger the bond the shortest is its size.

Single, double, and triple bond lengths are listed in order.

$(C \equiv C) < (C = C) < (C - C)$

**2. Which of the following have identical bond orders?**

**(I) $CN^-$** **(II) $NO^+$**

**(III) $O_2^-$** **(IV) $O_2^{2-}$**

**Select the correct option.**

**(a) (I) and (II)** **(b) (I) and (III)**

**(c) (II) and (III)** **(d) (III) and (IV)**

**[NCERT Exemplar]**

**Ans.** *(a) (I) and (II)*

**Explanation:** To find the identical bond orders we need to calculate the number of electrons:

$CN^- = 6 + 7 + 1 = 14$

$NO^+ = 7 + 8 - 1 = 14$

$O_2^- = 8 + 8 + 1 = 17$

$O_2^{2-} = 8 + 8 + 2 = 18$

### Related Theory

- *Isoelectronic molecules or ions have the same bond order.*
  *For example: $F_2$ and $O_2^{-2}$ (18 electrons) have bond order 1.*

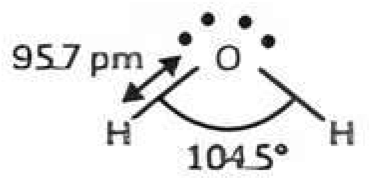
**3. The actual bond angle in $H_2O$ is:**

**(a) 120°** **(b) 104.5°**

**(c) 109.5°** **(d) 107°**

**Ans.** *(b) 104.5°*

**Explanation:** Because of the presence of two lone pairs on the oxygen atom, there is a repulsion between the electrons. Due to this the lone pair slightly pushes the hydrogen atom and the bond angle comes slightly less than 109.5° i.e., it is 104.5°.



**4. The dipole moment depends primarily on the electronegativity of the constituent atoms and shape of a molecule. Which of the following has the highest dipole moment?**

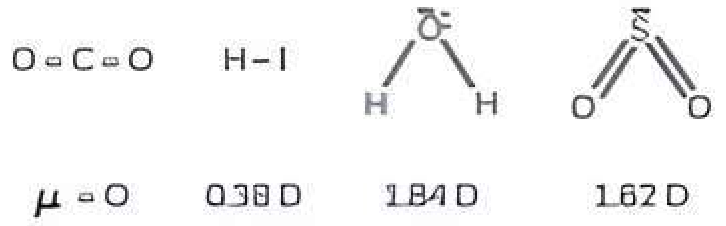
**(a) $CO_2$** **(b) HI**

**(c) $H_2O$** **(d) $SO_2$**

**Ans.** *(c) $H_2O$*

**Explanation:** $CO_2$ being symmetrical has zero dipole moment.

Among HI, $H_2O$ and $SO_2$, dipole moment is highest for $H_2O$ as in $H_2O$ the central atom oxygen contains two lone pairs while in $SO_2$, sulphur contains one lone pair.



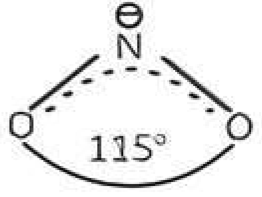
**5. ONO bond angle is minimum in:**

**(a) $NO_3^-$** **(b) $NO_2^-$**

**(c) $NO_3^-$** **(d) $NO_2^+$**

**Ans.** *(b) $NO_2^-$*

**Explanation:** ONO Bond angle in $NO_3^-$ is 120°. ONO Bond angle in $NO_2^-$ is 115°. ONO Bond angle in $NO_2$ is 132°. ONO Bond angle in $NO_2^+$ is 180°. So, the bond angle is minimum in $NO_2^-$ as shown in the figure:



6. The resonance structure of a molecule should not have:

(a) nearly the same energy content

(b) identical arrangements of atoms

(c) the same number of paired electrons

(d) identical bonding

**Ans** *(d) identical bonding*

**Explanation:** Resonance structure does not have identical bonding. Resonance involves the delocalisation of π-electrons.

It is a concept in which two or more alternate valence bond structures are written for a molecule. They have almost the same energy levels and the structures have identical arrangements of atoms.

7. The correct stability order of the following resononce structure is:

(I) $H_2C = \overset{+}{N} = \overset{-}{N}$ (II) $H_2\overset{+}{C} - N = \overset{-}{N}$

(III) $H_2\overset{-}{C} - \overset{+}{N} \equiv N$ (IV) $H_2\overset{-}{C} = N = \overset{+}{N}$

Select the correct option.

(a) (I) > (III) > (II) > (IV)

(b) (I) > (II) > (III) > (IV)

(c) (I) > (III) > (IV) > (II)

(d) (IV) > (III) > (II) > (I)

**Ans.** *(a)* (I) > (III) > (II) > (IV)

**Explanation:** Stability of resonance structures are decided by following factors:

(1) Neutral molecules are more stable.

(2) Greater the number of covalent bonds, more will be its stability.

(3) Structures with a negative charge on more electronegative atom will be more stable.

(4) Like charges should be at maximum distance.

### Related Theory

- *Points for the estimation of stability in resonating structures:*

  *(1) Greater the number of covalent bonds, the greater is stability.*

  *(2) Less the number of formal charges more is the stability.*

  *(3) Negative charge on more electronegative atoms is more stable and vice versa.*

  *(4) Equivalent resonance forms have no difference in stability. They contribute equally.*

8. Which of the following statements is correct?

(a) $F_2O$ is linear in shape.

(b) $H_2O$ is bent in shape.

(c) $F_2O$ is bent in shape.

(d) Both (b) and (c)

**Ans.** *(d) Both (b) and (c)*

**Explanation:** Both $F_2O$ and $H_2O$ are bent in shape because of the lone pair-lone pair repulsion between the atoms.

### Caution

- *Students should know that shape of $H_2O$ is bent or V-shape due to the presence of two lone pairs.*

9. The bond angle in $NF_3$ (102.3)° is smaller than $NH_3$ (107.2)°. This is because of:

(a) large size of F compared to H

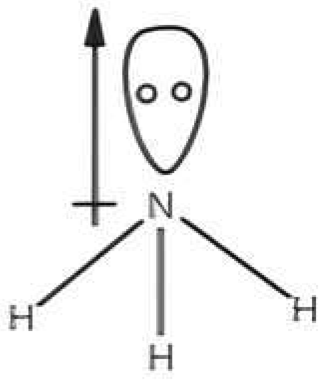
(b) large size of N compared to F

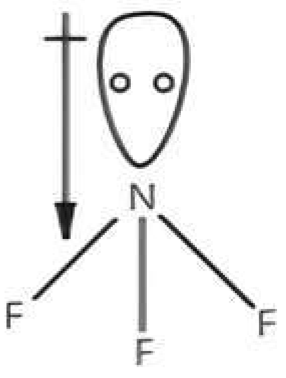
(c) opposite polarity of N in the two molecules

(d) small size of H compared to N

**Ans.** *(c) opposite polarity of N in the two molecules*

**Explanation:**





In $NH_3$, 'N' is more electronegative and only *lp-bp* repulsion is present but in the case of $NF_3$, 'N' is less electronegative than 'F' and there is *lp-lp* repulsion between N and F lone pair of electrons. As a result, bond angle decreases in case of $NF_3$.

## Assertion-Reason (A-R)

In the following question no. (10–13) a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choice.

(a) Both (A) and (R) are true and (R) is the correct explanation of (A).

(b) Both (A) and (R) are true but (R) is not the correct explanation of (A).

(c) (A) is true but (R) is false.

(d) (A) is false but (R) is true.

10. 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 the nitrogen atom has one lone pair and the oxygen atom has two lone pairs. [NCERT Exemplar]

**Ans.** *(a) Both (A) and (R) are true and (R) is the correct explanation of (A).*

**Explanation:** Lone pairs produce more repulsion than bond pairs. So, the angle will decrease with the increase in repulsion. In this case, nitrogen has one lone pair and oxygen has two lone pairs. Because of the presence of two lone pairs in oxygen bond angle of $H_2O$ will be less compared to that of $NH_3$.

**11. 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 (R):** **The electronic environment around oxygen is the same even after the breakage of one O–H bond.**

**Ans.** *(d) (A) is false but (R) is true.*

**Explanation:** To break the different bonds in the same molecule, different energies are given. So, for breaking the first and second O–H bonds in $H_2O$ molecule different energies are given. The electronic environment around the oxygen will change after breaking one of the O–H bonds.

**12. Assertion (A):** **The dipole moment helps to predict whether the molecule is polar or non-polar.**

**Reason (R):** **The dipole moment helps to predict the geometry of molecules.**

**Ans.** *(a) Both (A) and (R) are true and (R) is the correct explanation of (A).*

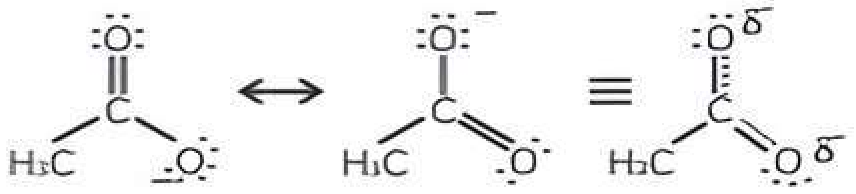
**Explanation:** The linear triatomic molecule like $CO_2$ have no dipole moment because the two bond moment (polarity) cancel each other. Therefore, geometry of molecule can be predicted by the value of dipole moment.

**13. Assertion (A):** **Both carbon and oxygen bond lengths are equal in acetate ion.**

**Reason (R):** **Bond length decreases with the multiplicity of bond between two atoms.**

**Ans.** *(b) Both (A) and (R) are true but (R) is not the correct explanation of (A).*

**Explanation:** Due to the resonance in acetate ion, the negative charge spreads over the molecule equally and hence, they have equal carbon and oxygen bond length.



Bond length decreases with the multiplicity of bond between two atoms. For example: bond length of ethane > ethene > ethyne.

So, both the assertion and reason are true but the reason does not explain the assertion correctly.

## CASE BASED Questions (CBQs)

[ **4** & **5** marks ]

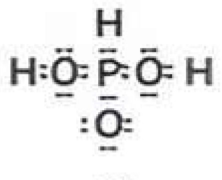
**Read the following passages and answer the questions that follow:**

**14.** *Bond energy is the amount of energy required to break any bond in a molecule. It is observed that the shorter the bond length greater is the bond energy. Bond energy increases with the increasing bond order. It also decreases with the increase in lone pairs on the bonded atom due to the electrostatic repulsion of lone pairs on the two bonded atoms. Bond energy is affected by the resonance. In the case of similar molecules, down the group, the bond energy decreases. According to the concept of resonance, when a single Lewis structure cannot define a molecule properly then a number of structures with the almost same energy and the same position of nuclei are taken as a canonical structures. Resonance stabilizes the molecule as the energy of the resonance hybrid is less and lies between the canonical structure. As the result of resonance, the bond order changes in many molecules or ions.*

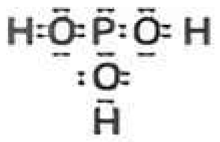
**(A) Arrange these in the bond energy order.**

**$C \equiv C$**
**$C=C$**
**$C-C$**

**(B) $H_3PO_3$ can be represented by structures 1 and 2 shown below. Can these two structures be taken as the canonical forms of the resonance hybrid representing $H_3PO_3$? If not, give reasons for the same.**



(1)



(2)

**[NCERT]**

**(C) Answer the following questions:**

**(i) Compare the bond energy in $Cl_2$, $N_2$, and $O_2$.**

**(ii) Find the average bond energy of O–H bond in $H_2O$ molecule.**

**Ans.** (A) The order of bond energy is

$$C \equiv C > C = C > C - C$$

Multiple bonds have more bond energy than the single bond.

### Related Theory

- *The length of a double bond is less than the length of a single and the length of a triple bond is even shorter than a double bond.*

*Triple < double < single*

(B) As the position of atoms has been changed in the given structures, thus these cannot be taken as the canonical forms of the resonance hybrid of $H_3PO_3$.

(C) (i) The bond energy in $Cl_2$, $N_2$ and $O_2$ can be calculated by the presence of a number of lone pairs.

$$\text{Bond energy} = \frac{1}{\text{Bond order}}$$

Cl—Cl has one bond.

O—O has two bond order.

N—N has three bond order.

So, the order of bond energy will be N—N > O—O > Cl—Cl

(ii) In $H_2O$ molecule:

$H{-}O{-}H_{(g)} \rightarrow 2H_{(g)} + O_{(g)}; \Delta H = 926 \text{ kJmol}^{-1}$

The average bond energy of the O—H bond

$$= \frac{926}{2}$$

$$= 463 \text{ kJmol}^{-1}$$

**15.** *The bond angle of a molecule depends on hybridisation, lone pair repulsion and electronegativity of a molecule. The lone pair of a molecule always tries to repel the bonded pair of electrons. Because of this, a slight increase is seen in the angle of the respective atom. The bond angle increases with a decrease in the electronegativity if the central atom is the same for different molecules. It also depends on the state of hybridisation of the central atom. The geometry of a molecule is also predicted by the dipole moment. A symmetrical molecule shows zero dipole moment. Molecules having zero dipole moments are called non-polar molecules and the molecules having $\mu \neq 0$ are called polar molecules.*

**(A) The actual bond angle of $NH_3$ is:**

**(a) 105°** **(b) 106.7°**
**(c) 110.95°** **(d) 102°**

**(B) Compare the bond angle between $NH_3$, $PH_3$ and $AsH_3$.**

**(a) $NH_3 > PH_3 > AsH_3$**
**(b) $NH_3 < PH_3 < AsH_3$**
**(c) $NH_3 < AsH_3 < PH_3$**
**(d) $PH_3 < AsH_3 < NH_3$**

**(C) Identify the correct statement regarding $NH_3$ and $BF_3$.**

**(a) Both are Lewis acid**
**(b) Both are isostructural**
**(c) Both are Lewis base**
**(d) Have different values of dipole moment [Delhi Gov. QB 2022]**

**(D) The $SCl_2$ molecule has a bent shape and is not linear because of:**

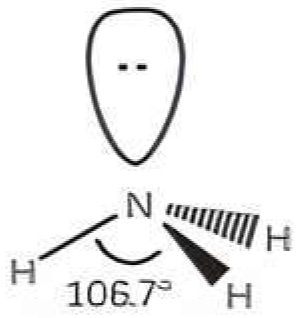
**(a) presence of two lone pairs at sulphur atom**
**(b) presence of four lone pairs at sulphur atom**
**(c) do not have a bent shape**
**(d) the size of sulphur atom is smaller than chlorine**

**(E) The bond angle .................. with the decrease in electronegativity.**

**(a) increases**
**(b) decreases**
**(c) first increases then decrease**
**(d) remains constant**

**Ans.** (A) *(b) 106.7°*

**Explanation:** The actual bond angle of $NH_3$ is 106.7°.



(B) *(a) $NH_3 > PH_3 > AsH_3$*

**Explanation:** The bond angle depends upon the electronegativity of the central atom. Bond angle decreases with the decrease in electronegativity.

$$NH_3 > PH_3 > AsH_3$$
$$107° \quad 93° \quad 91.48°$$

### Related Theory

- ***Lone pair repulsion:*** *As the lone pair of electrons on the atom increases, it creates repulsion between the bonded pair of electrons which simultaneously decreases the bond angle.*

***Electronegativity:*** *Bond angle increases with decreases in electronegativity of surrounding atoms in the molecules having the same central atom.*

(C) *(d) Have different values of dipole moment.*

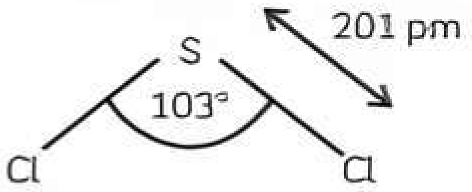
**Explanation:** $NH_3$ is a Lewis base as it has lone pair of electrons to donate while $BF_3$ is a Lewis acid as its octet is not complete and it is ready to accept the electrons.

$NH_3$ is trigonal pyramidal due to the presence of a lone pair while $BF_3$ is trigonal planar.

$BF_3$ has zero dipole moment as it has a symmetrical structure while $NH_3$ has a dipole moment of 1.4 D.

(D) *(a) presence of two lone pairs at sulphur atom.*

**Explanation:** The $SCl_2$ molecules have a bent shape and are not linear because of the presence of two lone pairs of electrons at the sulphur atom. The chlorine atoms and lone pairs repel each other. This gives a bent shape to $SCl_2$ molecule.



(E) *(a) increases*

**Explanation:** The bond angle is inversely proportional to the substituents' electronegativity. A more electronegative substituent attracts electrons, lowering the charge density on the central atom. As a result, the bond angle decreases.

## VERY SHORT ANSWER Type Questions (VSA)

[ 1 mark ]

**16. How is the resonance energy related to the stability of the molecule? [Diksha]**

**Ans.** The resonance allows the delocalisation of the pi-bond. Because the electron occupies a vast space, the overall energy of a molecule is reduced. So, if the molecule possesses any resonating structures, it is the most stable. The higher the resonance energy, the more stable the molecule.

**17. How do electron dot structures (Lewis structures) relate to the bond angle?**

**Ans.** Bond angle is the shortest angle between one bond and another bond. This is driven by the electrons in the bonds and lone pairs of the central atom repelling each other and trying to maintain the further distance as apart as possible.

**18. Give a reason why the dipole moment of $CCl_4$ is zero.**

**Ans.** In $CCl_4$ the dipole moment is zero although the C–Cl bonds are polar, this is because the shape of the molecule is tetrahedral and due to this the molecule is symmetrical. Hence, the individual dipole moment of polar bonds cancels out each other and the resultant dipole is zero.

**19. Define bond angle and the factors on which it depends.**

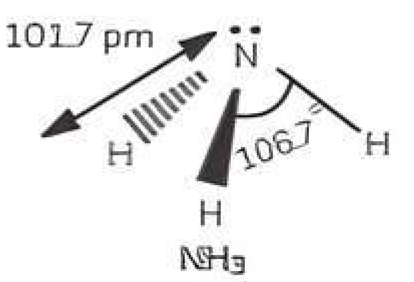
**Ans.** Bond angle is the angle between two adjacent bonds of an atom of the same molecule. The factors on which bond angle depends are: Hybridisation, lone pair–bond pair repulsion, and electronegativity.

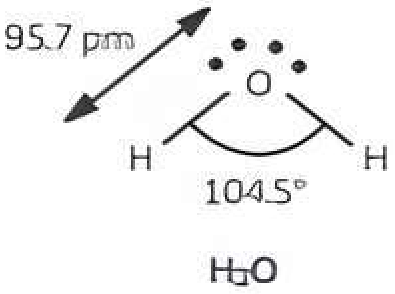
## SHORT ANSWER Type-I Questions (SA-I)

[ 2 marks ]

**20. The bond angles of $NH_3$ and $H_2O$ molecules are shorter than the normal tetrahedral angles. Explain:**

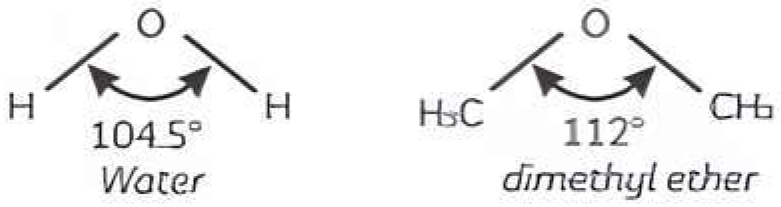
**Ans.** The bond angle of $NH_3$ and $H_2O$ molecules are shorter than the normal tetrahedral angles because of the presence of one lone pair of electrons on nitrogen atom in $NH_3$ and two lone pairs on the oxygen atom of $H_2O$, which causes lone pair–bond pair and lone pair-lone pair repulsion between the atoms.





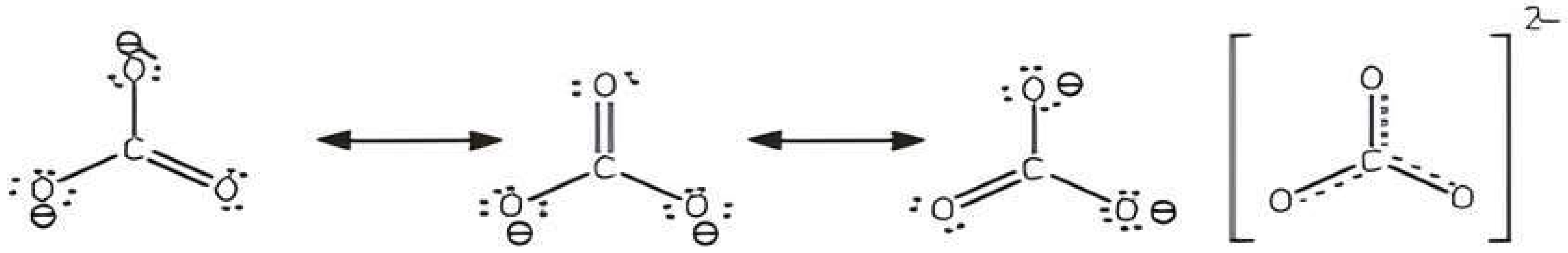
**21. In both water and dimethyl ether $CH_3$—O—$CH_3$, an oxygen atom is a central atom yet they have different bond angles. Which one has a greater bond angle? Give a reason. [NCERT Exemplar]**

**Ans.** Dimethyl ether has a greater bond angle as compared to water. In both the molecules the central atom is oxygen, having two lone pairs of electrons. The bond angle of dimethyl ether is greater because of the more repulsion between the two bulky groups (methyl) as compared to that of the H atoms in water.



**22. All the C—O bonds in carbonate ion $CO_3^{-2}$ are equal in length. Explain.**

**Ans.** In $CO_3^{-2}$, all the bonds are equal because the bonds are not fixed and hence, they show resonance.

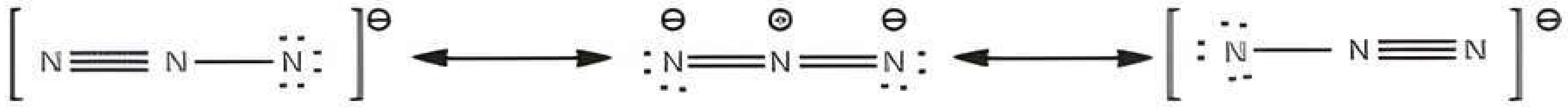


Resonance structures of carbonate ion

Resonance hybrid

**23. Write the resonating structure of $N_3^-$.**

**Ans.** Azide ions ($N_3^-$) have three resonating structures.



## SHORT ANSWER Type-II Questions (SA-II)

[ **3** marks ]

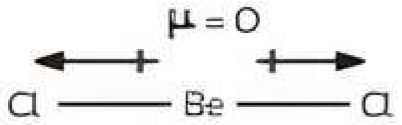
**24. Explain why $BeCl_2$ has zero dipole moment.**

**Ans.** $BeCl_2$ has zero dipole moment because:

(1) $BeCl_2$ is symmetrical due to its linear shape.

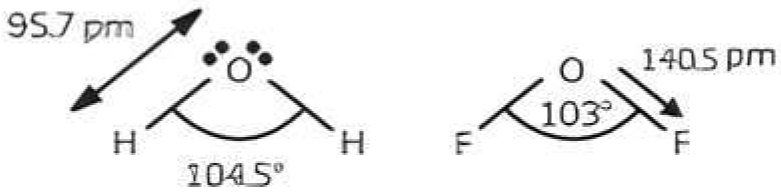
(2) It is a non-polar molecule.

(3) In $BeCl_2$ molecule, the equal and opposite Be—Cl bonds cancel their individual dipole moment and the net dipole comes to be zero.



**25. Why the bond angle of $H_2O$ is more than that of $F_2O$?**

**Ans.** In both $H_2O$ and $F_2O$, the central atom is oxygen. Fluorine has a higher electronegativity than oxygen. Due to this, the shared pair of electrons shifts towards the fluorine and decreases the electron density on the central atom. While in the case of $H_2O$, the electrons shift towards the oxygen. So, $F_2O$ has very little tendency to open up the angle. But in $H_2O$ this opening up is more as the bond pair electrons are closer to each other. Hence, bond angle of $F_2O$ is less than $H_2O$.

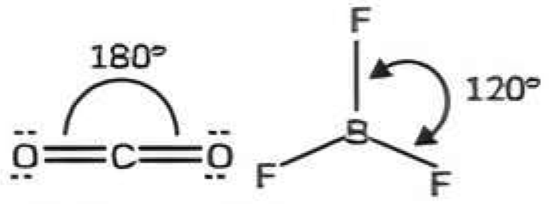


**26. Which of the following in each pair has a larger bond angle?**

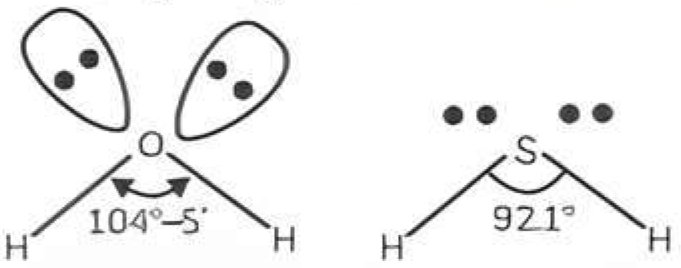
**[Delhi Gov. QB 2022]**

**(A) $CO_2$, $BF_3$ (B) $H_2O$, $H_2S$ (C) $CH_4$, $C_2H_2$.**

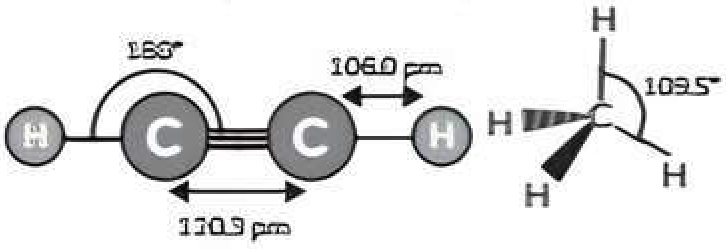
**Ans.** (A) $CO_2$ has larger bond angle than $BF_3$.



(B) $H_2O$ has a higher bond angle as bond angle increases with an increase in electronegativity of central atom.



(C) $C_2H_2$ has higher bond angle than $CH_4$.



## LONG ANSWER Type Questions (LA)

[ **4** & **5** marks ]

**27. What is a dipole moment? Write its significance.**

**Ans.** The product of magnitude of positive and negative charges and the distance between their dipoles are known as dipole moment. Mathematically it is expressed as:

$$\mu = q \times d$$

Here, $\mu$ is the dipole moment, q is the magnitude of the charge and $d$ is the nuclear distance Dipole moment is expressed in Debye (D).

Significance of dipole moment are:

(1) It is used to determine the polarity of a molecule.

Molecules having zero dipole moment are said to be non-polar molecules while those with $\mu \neq 0$ are called polar molecules.

(2) Its values are used to determine the percentage ionic character in a molecule.

The percentage ionic character for a bond can be calculated with the help of a dipole moment. Its general formula is:

% ionic character

$$= \frac{\text{experimental value of dipole moment}}{\text{theoretical value of dipole moment}} \times 100$$

(3) It is used to determine the geometry of molecules.

The value of dipole moments helps to determine the molecular structure. For example:

(i) In $H_2O$ the dipole moment of molecule is non-zero. So, it has a V-Shaped structure and bond angle is 105°. Similarly, $SO_2$ also have a bent structure.

(ii) In $CO_2$, the dipole moment is zero so it has a linear shape.

**28. What is meant by the term average bond enthalpy? Why is there a difference in bond enthalpy of O–H bond in ethanol and water? [NCERT Exemplar]**

**Ans.** The bond dissociation enthalpy is divided by the number of bonds broken to get the average bond enthalpy.

All the similar bonds in a molecule do not have the same bond enthalpies. The average bond enthalpy is determined for bond strength calculations in polyatomic molecules like $H_2O$, $CH_4$, $C_2H_5OH$ etc.

In case of $H_2O$: $H-O-H_{(g)} \rightarrow 2H_{(g)} + O_{(g)}$

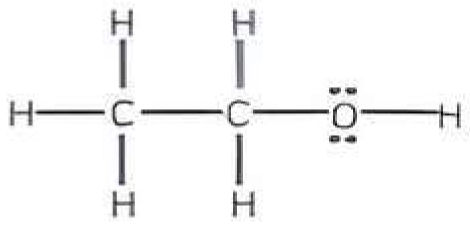
$\Delta H = 926 \text{ kJmol}^{-1}$

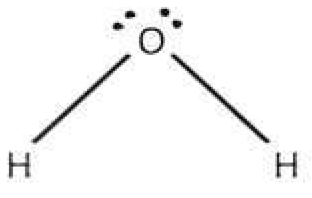
The average bond energy of the O—H bond is:

$$= \frac{926}{2}$$

$$= 463 \text{ kJ mol}^{-1}.$$

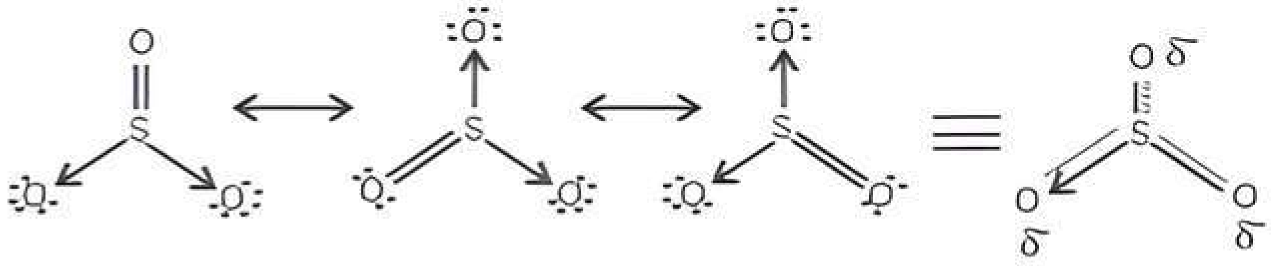
The bond enthalpy of O–H bond in $C_2H_2OH$ and $H_2O$ are different because of the different chemical (electronic) environment around oxygen atoms. In $C_2H_5OH$, the O–H bond is attached with carbon while that in $H_2O$, the O–H the bond is attached with hydrogen, as shown in the figure below.



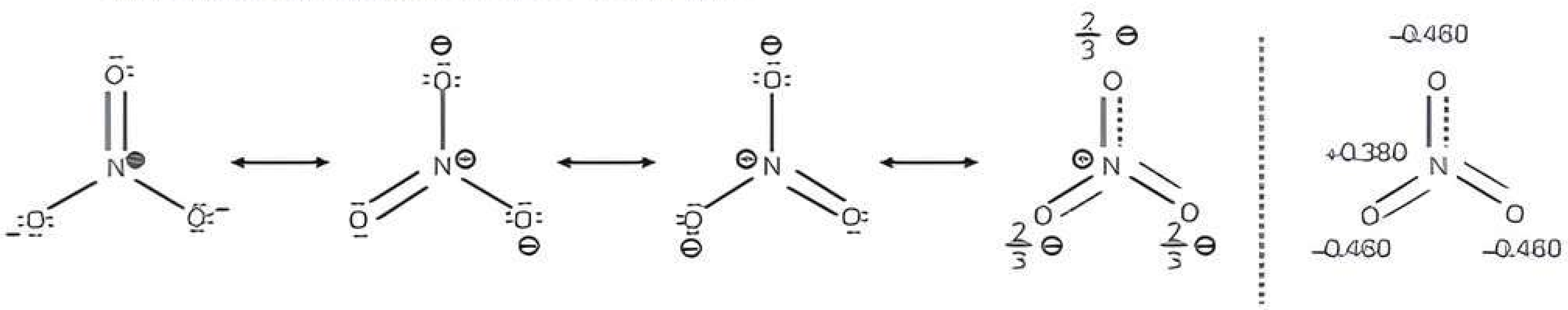


**29. Write the resonating structures of $SO_3$, $NO_3^-$ and ozone.**

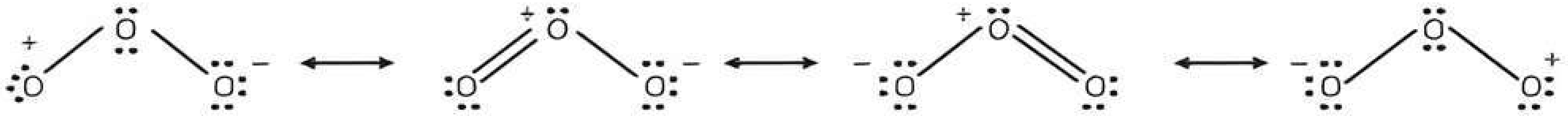
**Ans.** The resonating structure of $SO_3$ is as follows:



The resonating structure of $NO_3^-$ is as follows.



The resonating structure of ozone $(O_3)$ is as follows.



# THEORIES OF CHEMICAL BONDING 3

## TOPIC 1

## VALENCE SHELL ELECTRON PAIR REPULSION (VSEPR) THEORY

Although lewis's concept explained the structure of several molecules but could not predict the shapes of the molecules in many cases. In order to explain the shapes of molecules adequately, Sidgwick and Powell in 1940 proposed a valence shell electron pair repulsion theory based on the repulsive interaction of the electron pairs in the valence shell of the atoms.

### Postulates of VSEPR Theory

(1) The molecules are made up of different types of atoms, one of which is a central atom.

(2) The shape of a molecule depends upon the number of electron pairs in the valence shell which includes bonded or non-bonded electrons around the central atom.

(3) The electron pairs repel each other since the electron clouds are negatively charged.

(4) The electron pair tends to be in the maximum distance so that the repulsion between the electrons will be minimum.

(5) The valence shell is taken as a sphere where the electron pairs are localising on the spherical surface which will be at a maximum distance.

(6) The single or double or triple electron pairs are counted as only one electron pair.

(7) The VSEPR theory is also applicable to molecules that have two or more resonance structures.

The electron pair that takes part in the bonding is called bond pair (bp) and the electron pair that does not take part in the bonding is called lone pair (lp).

(8) The repulsive interaction of electron pairs decreases in the given order:

Lone pair – lone pair > lone pair – bond pair > bond pair – bond pair

### Refined Theory

(1) Nyholm and Gillespie refined the VSEPR theory and explained the important difference between the lone pairs and bond pairs. The lone pairs are localised on the central atom and bond pairs are shared between two atoms.

(2) The lone pair occupies more space than bonding pairs of electrons. So, there is a greater repulsion between lone pairs as compared to bonding pairs of electrons.

(3) This repulsion affects the idealised shapes of the molecules and deviation in bond angles occurs.

(4) The VSEPR theory divides molecules into two types:

   (i) The molecules in which the central atom has no lone pair of electrons.

   (ii) The molecules in which the central atom has one or more lone pairs of electrons.

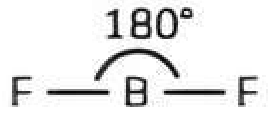
(5) The VSEPR theory predicts the geometry of the various molecules, especially element geometry. It is also useful in determining the geometry of the molecules even if their different possible structures have smaller energy differences. The VSEPR theory is a theoretical one that cannot explain certain molecular shapes.

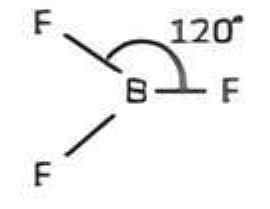
(6) When lone pairs of an electron are present then the ideal shape of the molecules gets distorted.

Table: Molecules having geometry with no lone pair of electrons

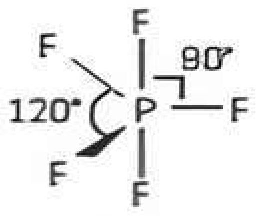
| Molecule type | Ideal shape | Example |
|---|---|---|
| $AB_2$ | Linear | $BeCl_2$ |
| $AB_3$ | Trigonal planar | $BF_3$ |
| $AB_4$ | Tetrahedral | $CH_4$ |
| $AB_5$ | Pentagonal bipyramidal | $PCl_5$ |
| $AB_6$ | Octahedral | $SF_6$ |

Linear

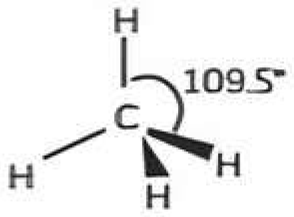




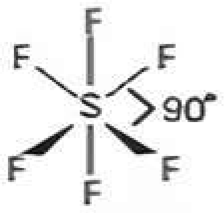
Trigonal Planar



Trigonal Bi-pyramidal

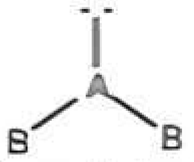
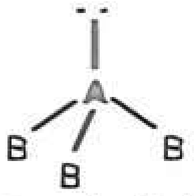
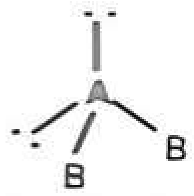
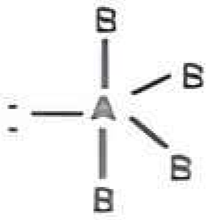
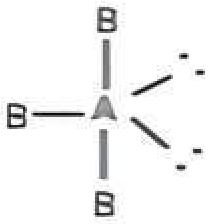
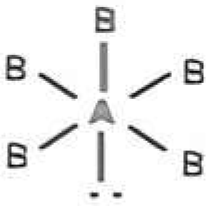
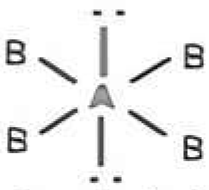


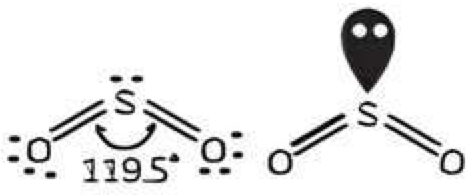
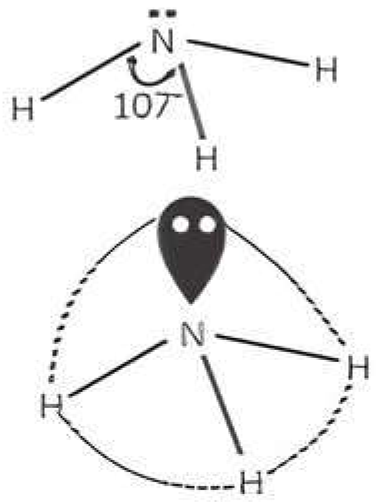
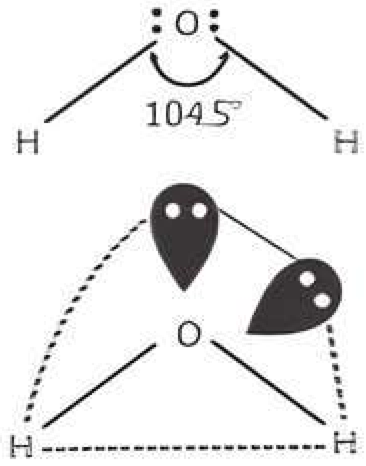
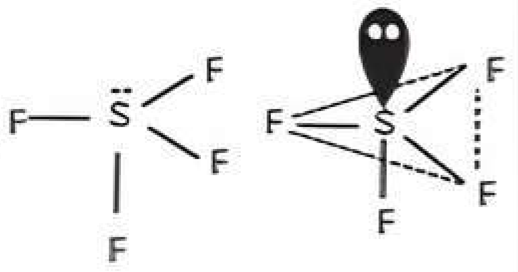
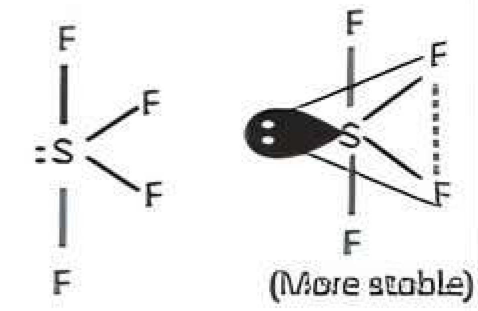
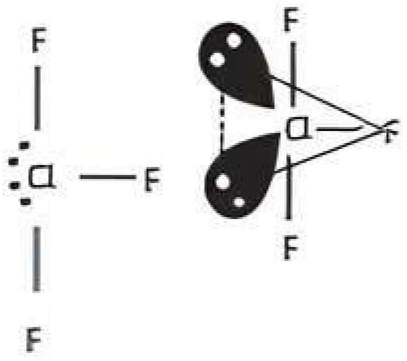
Tetrahedral

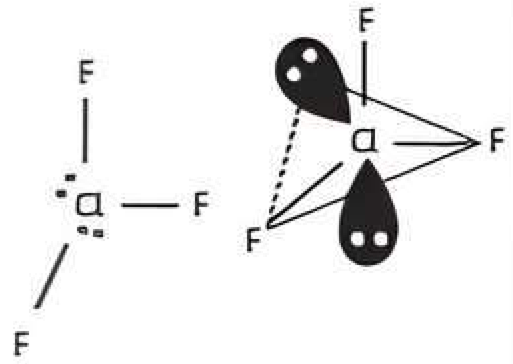
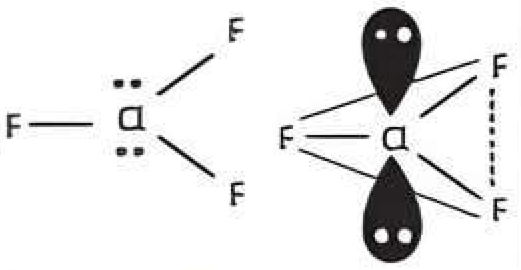


Octahedral

Table: Molecules having both bond pair and lone pair of electrons

| Molecule type | No. of bonding pairs | No. of lone pairs | Arrangement of electron pairs | Shape | Examples |
|---|---|---|---|---|---|
| $AB_2E$ | 2 | 1 | <br>Trigonal planar | Bent | $SO_2$, $O_3$ |
| $AB_3E$ | 3 | 1 | <br>Tetrahedral | Trigonal Pyramidal | $NH_3$ |
| $AB_2E_2$ | 2 | 2 | <br>Tetrahedral | Bent | $H_2O$ |
| $AB_4E$ | 4 | 1 | <br>Trigonal bi-pyramidal | See-saw | $SF_4$ |
| $AB_3E_2$ | 3 | 2 | <br>Trigonal bi-pyramidal | T-shape | $ClF_3$ |
| $AB_5E$ | 5 | 1 | <br>Octahedral | Square pyramidal | $BrF_5$ |
| $AB_4E_2$ | 4 | 2 | <br>Octahedral | Square planar | $XeF_4$ |

| Molecule type | No. of bonding pairs | No. of lone pairs | Arrangement of electron pairs | Shape | Reason for the shape acquired |
|---|---|---|---|---|---|
| $AB_2E$ | 4 | 1 |  | Bent | Theoretically the shape should have been triangular planar but actually it is found to be bent or V-shaped. The reason for this is the lone pair-bond pair repulsion is much more as compared to the bond pair-bond repulsion. So the angle is reduced to 119.5 from 120. |
| $AB_3E$ | 3 | 1 |  | Trigonal Pyramidal | As there is one lone pair present and due to the repulsion between lp-bp the angle between bond pairs is reduced to 107° from 109.5°. |
| $AB_2E_2$ | 2 | 2 |  | Bent | The shape should have been tetrahedral if there were all bp but two lp are present so the shape is distorted tetrahedral or angular. The reason is lp-lp repulsion which is more than lp-bp repulsion. Thus, the angle is reduced to 104.5° from 109.5°. |
| $AB_4E$ | 4 | 1 | (a)  (b)  (More stable) | See-saw | In (a) the lp is present at axial position so there are three lp-bp repulsions at 90° while in (b) the lone pair is present at the equatorial position and there are two lp-bp repulsions. Hence, arrangement (b) is more stable. The shape shown in (b) is described as a distorted tetrahedron, a folded square or a see-saw. |
| $AB_3E_2$ | 3 | 2 | (a)  | T-shape | In (a) the lone pairs are at equatorial position so there are less lp-bp repulsions as compared to others in which the lone pairs are at axial positions. So structure (a) is the most stable (T-shaped). |

| Molecule type | No. of bonding pairs | No. of lone pairs | Arrangement of electron pairs | Shape | Reason for the shape acquired |
|---|---|---|---|---|---|
| | | | (b) <br> <br>(c) <br> | | |

**Important**

- Number of electron pair = $\frac{(V.E.+X)}{2}$

Where V.E = Valence electron and X number of atoms linked to central atom except S, O and N atoms.

Number of bond pairs = total number of bonds made by central atom

Number of lone pairs = total number of electron pairs – total number of bond pairs

For example: $BF_3$

Total electron pair = $\frac{3+3}{2} = 3$

Total bond pair is 3

Total lone pair is $3 - 3 = 0$

Hence, geometry of $BF_3$ is Trigonal planar.

**Example 3.1:** Case Based:

*VSEPR theory says that the shape of a molecule depends on the number of electron pairs in the valence shell which may be a bond pair or lone pair. The bond pairs are the pairs that take part in the bonding and the lone pair remains as the non-bonded electron pair.*

(A) The number of lone pairs present in the $BeCl_2$:

| | |
|---|---|
| (a) Zero | (b) One |
| (c) Two | (d) Three |

(B) Which of the following statements is incorrect about VSEPR theory?
  (a) It applies to the molecules having two or more resonance structures.
  (b) The lone pairs tend to be at a maximum distance.
  (c) The bond pair-bond pair has the highest repulsion.
  (d) The lone pair-lone pair has the highest repulsion

(C) Calculate the number of bond pairs and lone pairs present in the $ClF_3$ molecule?

(D) In $ClF_3$ which one is the central atom and also draw the structure of the molecule?

(E) Assertion (A): The $BrF_5$ molecule has a square pyramidal shape.

Reason (R): The shape is distorted due to the one lone pair electron.

  (a) Both (A) and (R) are true and (R) is the correct explanation of (A).
  (b) Both (A) and (R) are true but (R) is not the correct explanation of (A).
  (c) (A) is true but (R) is false.
  (d) (A) is false but (R) is true.

**Ans.** (A) *(a) Zero*

Explanation: Number of electron pair $= \frac{V.E.+X}{2}$ Where, V.E. = Valence electron and X = number of atoms linked to central atom except S, O and N atoms.

Number of bond pairs = total number of bonds made by central atom

Number of lone pairs = total number of electron pairs – total number of bond pairs

For $BeCl_2$,

No. of electron pair $= \frac{2+2}{2} = 2$

No. of lone pair $= 2 - 2 = 0$

(B) *(c) The bond pair-bond pair has the highest repulsion.*

Explanation: The bond pair-bond pair doesn't have maximum repulsion. It is having a minimum amount of repulsion. Other statements are correct about the VSEPR theory.

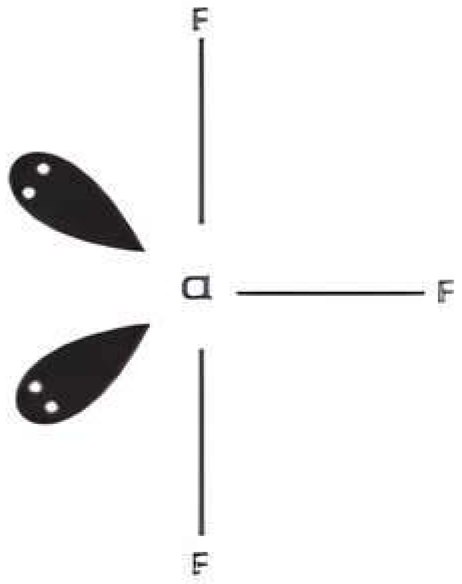
(C) No. of electron pair $= \frac{7+3}{2} = 5$

No. of bond pair = 3

No. of lone pair = No. of electron pair – No. of bond pair

$= 5 - 3 = 2$

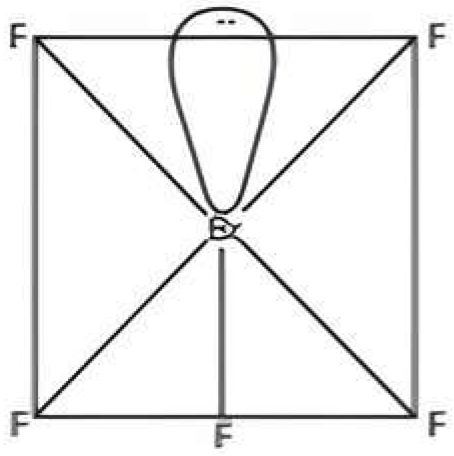
**(D)** In the $ClF_3$ molecule, the chlorine is the central atom with 7 electrons around it. It is having a T-Shaped molecular structure.



*Structure of $ClF_3$ molecule*

**(E)** *(a) Both (A) and (R) are true and (R) is the correct explanation of (A).*

**Explanation:** The $BrF_5$ molecule has five bond pairs and one lone pair of electrons which makes the structure distorted. So, both assertion and reason are correct and reason is the correct explanation of assertion.



*The Structure of $BrF_5$ molecule*

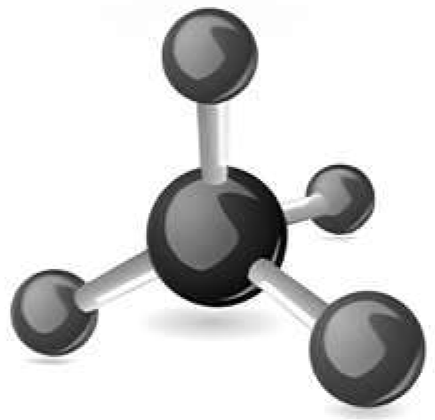
**Example 3.2:** **Discuss the shapes of the following molecules using the VSEPR model. [NCERT]**

**Ans.** $BeCl_2$, $BCl_3$, $SiCl_4$, $AsF_5$, $H_2S$ and $PH_3$

| Molecule | Number of electron pairs around central atom (Bond pair + lone pair) | Molecular Geometry | Bond Angle |
|---|---|---|---|
| $BeCl_2$ | Two (2+0) | Linear | 180° |
| $BCl_3$ | Three (3+0) | Trigonal Planar | 120° |
| $SiCl_4$ | Four (4+0) | Tetrahedral | 109.5° |
| $AsF_5$ | Five (5+0) | Trigonal bipyramidal | Three 109.5°.<br>Two 90°. |
| $H_2S$ | Six (2+2) | Non-Linear or Bent | 92° |
| $PH_3$ | Five (3+1) | Trigonal Pyramidal | 93.5° |

**Example 3.3:** **Apart from tetrahedral geometry, another possible geometry for $CH_4$ is square planar with the four hydrogen atoms at the corners of the square and the carbon atom at its centre. Explain why $CH_4$ is not square planar. [NCERT]**

**Ans.** According to the VSEPR theory, four bonded electron pairs around a carbon atom arranged themselves in regular tetrahedral geometry, in which bond angle is 109°28, while in a square planar structure, the bond angle is 90°. Therefore $CH_4$ can't be square planar because in square planar repulsion will be more. Hence, $CH_4$ is tetrahedral in shape.



*Geometry of methane molecule*

## Limitation of VSEPR Theory

Some significant limitations of the VSEPR theory include:

(1) This theory fails to explain isoelectronic species (i.e., elements having the same number of electrons). The species may vary in shape despite having the same number of electrons.

(2) The VSEPR theory does not shed any light on the compounds of transition metals. The structure of several such compounds cannot be correctly described by this theory. This is because the VSEPR theory does not take into account the associated sizes of the substituent groups and the lone pairs that are inactive.

(3) Another limitation of VSEPR theory is that it predicts that halides of group 2 elements will have a linear structure, whereas their actual structure is a bent one.

## TOPIC 2

# VALENCE BOND THEORY (VBT)

The theory was first proposed by Heitler and London (1927) and this theory was later developed by Pauling and others. The basic idea of VBT comes from atomic orbital, electronic configurations of elements, atomic orbitals overlap and variation and superposition principles. According to VBT, electrons in a molecule occupy atomic orbitals rather than molecular orbitals. The atomic orbitals overlap during the bond formation and the larger the overlap, the stronger is the bond. Let us consider the formation of a hydrogen molecule which is the simplest of all molecules.

Consider the two hydrogen atoms A and B. The nucleus of these atoms can be represented by $N_A$ and $N_B$ and the electrons in these atoms can be written as $e_A$ and $e_B$. When the two atoms are far apart there will be no interaction, when they are at a nearer distance then there will be some attractive and repulsive interactions between them.

The attractive forces can occur between:

The nucleus of an atom and its electron $N_A - e_A$ and $N_B - e_B$.

The nucleus of an atom and the other atom's electron $N_A - e_B$, $N_B - e_A$.

The repulsive force may occur between:

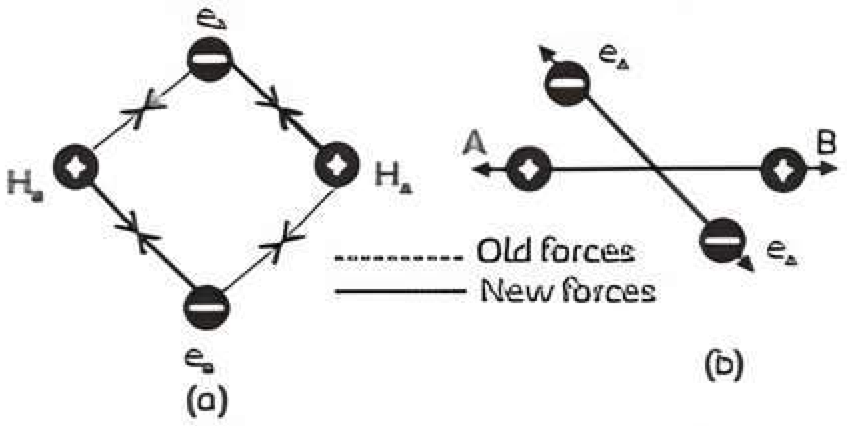
The electrons belong to two atoms $e_A - e_B$.

The nuclei belong to two atoms $N_A - N_B$.

The attractive force brings the two atoms close to each other, and repulsive force pushes them far away. The experimental results show that the magnitude is greater for attractive forces than repulsive forces. So, when the atoms approach closer, the potential energy decreases. At a particular time, the resultant attractive force balances the repulsive force and the system requires minimal energy. At this point, the hydrogen atoms get bonded together to form a stable molecule having a bond length of 74pm.

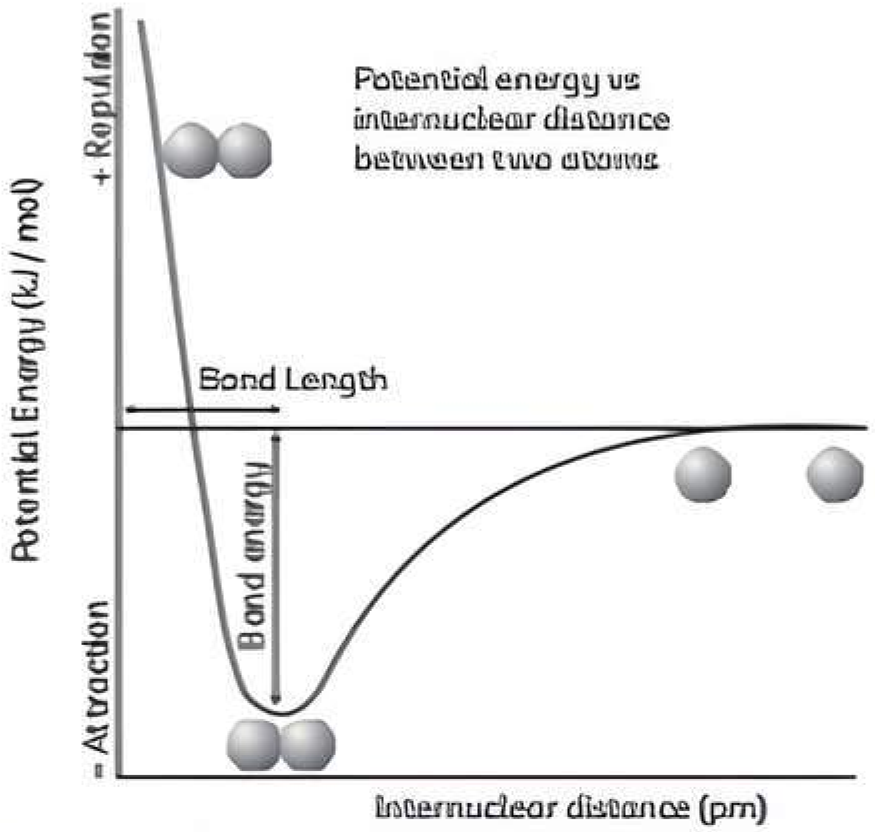
**Important**

- *During the formation of hydrogen molecules, the energy gets released which reflects that isolated atoms of hydrogen are less stable than a hydrogen molecule. The energy released during the formation of a molecule is called bond enthalpy. The energy required to dissociate one mole of a $H_2$ molecule is $H_{2(g)} + 435.8 \text{ kJ mol}^{-1} \rightarrow H_{(g)} + H_{(g)}$*



*(a) Forces of attraction during formation of hydrogen molecule*

*(b) Forces of repulsion during $H_2$ molecule formation*



*The potential energy diagram for $H_2$ molecule formation*

## TOPIC 3

# ORBITAL OVERLAP CONCEPT

During the formation of a molecule, there exists minimum energy which corresponds to two hydrogen atoms that are very close to each other at that point, the atomic orbitals of hydrogen atoms can undergo partial inter merging of orbitals which are called overlapping of atomic orbitals that makes the electron to pair up. The extent of overlap is directly proportional to the strength of a covalent bond. The greater the overlap between the atomic orbitals, the greater is their covalent bond strength. Therefore, 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.

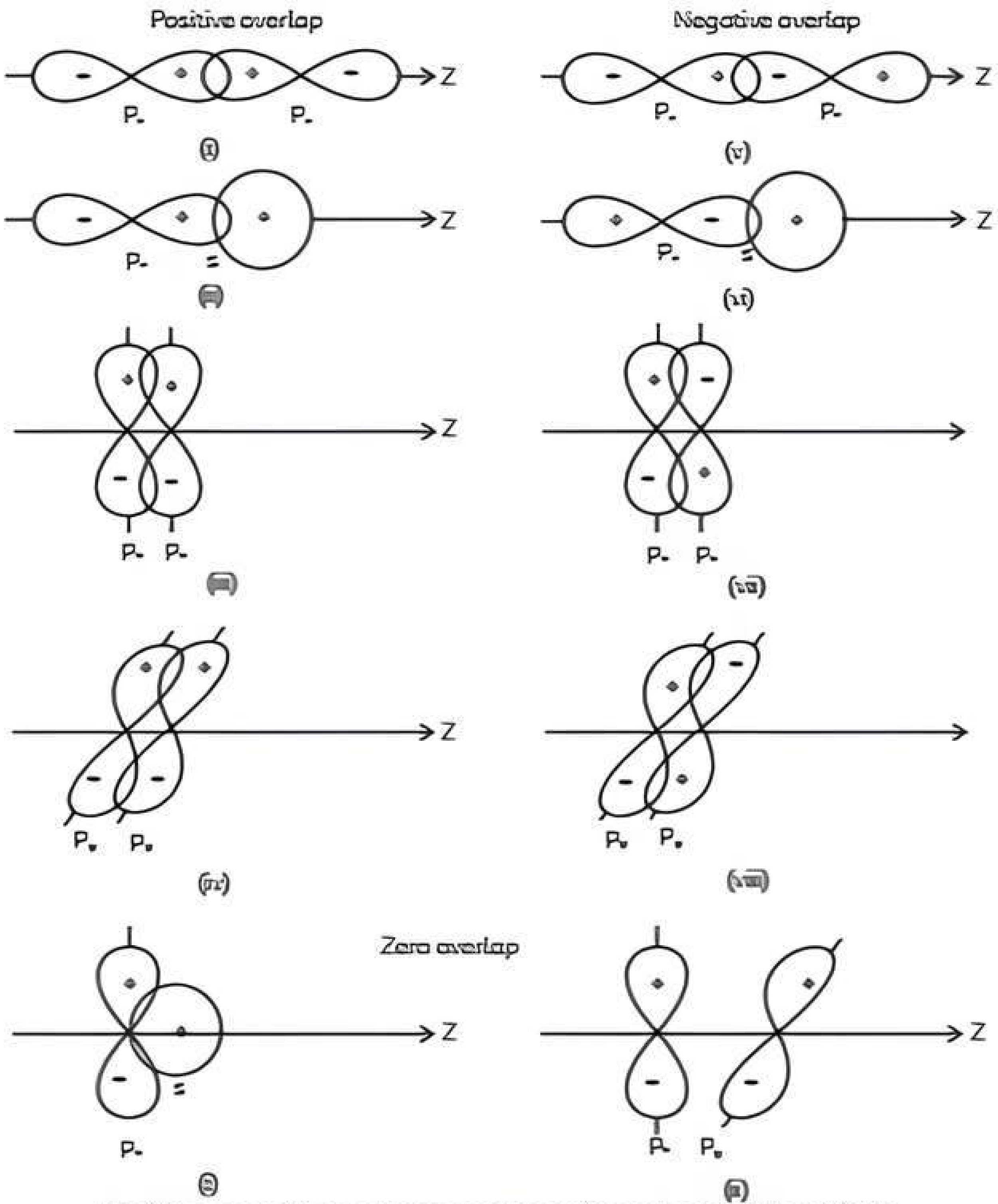
## Directional Properties of Bonds

When two atomic orbitals of atoms overlap, it will form a molecule with a covalent bond. The VBT explains the molecular shapes, their formation and directional properties of bonds in polyatomic molecules like $CH_4$, $NH_3$, $H_2O$ etc. in terms of overlap and hybridisation of atomic orbitals.

## Overlapping of Atomic Orbitals

The overlapping of two atomic orbitals may be positive, negative or zero depending on the sign (phase) and direction of orientation of amplitude of orbital wave function in space. Positive and negative signs on the boundary surface show the phase of the orbital wave function and it does not depend on the charge. When the two atomic orbitals forming a bond have the same phase and orientation it is called positive overlap. The overlap concept is the main factor for the formation of covalent bonds in the case of homonuclear or heteronuclear diatomic and polyatomic molecules. The $CH_4$, $NH_4$ and $H_2O$ have tetrahedral, pyramidal & bent shapes.

**Example:** The carbon has the electronic configuration in its ground state [He] $2s^2 2p^2$ when it is excited it has the electronic configuration of [He] $2s^1 2p^1_x\ 2p^1_y\ 2p^1_z$. The energy required for the excitation of electrons is equally compensated by the energy released during the overlap of orbitals ($p$) of carbon and hydrogen. The four atomic orbitals of carbon-containing unpaired electrons overlap with the 1s orbital of four H-atoms to form 4 C – H single bonds. The three orbitals of carbon are at 90° to one another the HCH has an angle of 90°. This indicates that three C–H bonds are oriented at 90° to one another. The shape of the 2s-orbital of carbon and 1s-orbital of hydrogen is spherically symmetrical allowing them to overlap in any direction. The direction of the fourth C–H bond cannot be found. These results are not matching with the tetrahedral HCH angles of 109.5°. This shows that simpler atoms overlapping does not give the directional properties of bonds in $CH_4$. Likewise, in $NH_3$ and $H_2O$ molecules the HNH and HOH angles should be 90°. This is not in agreement with the actual bond angle of 107° and 104.5° in $NH_3$ and $H_2O$ respectively.



*Positive, negative and zero overlaps of s and p-atomic orbitals.*

### Types of overlapping and nature of covalent bond

The covalent bond is classified into two types based on the overlapping of orbitals, they are:

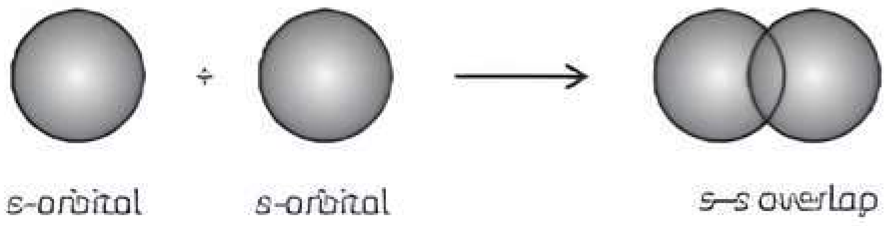
(1) Sigma bond (σ)

(2) pi-bond (π)

#### (1) Sigma bond

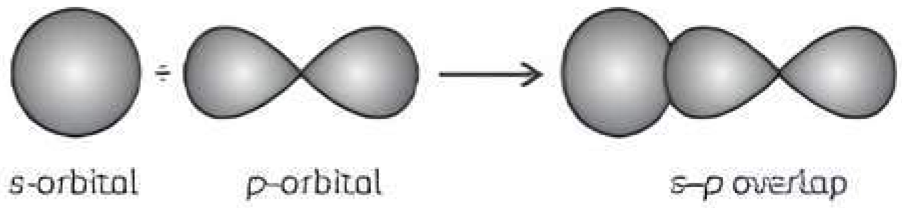
The sigma bond is formed by the end-to-end overlap of orbitals on its internuclear axis. This type of overlap is called axial overlap or head-on overlap. This bond can be formed from the following type of combination of atomic orbitals.

**s–s Overlapping:** When two half-filled s-orbital overlap along the internuclear axis, it is called s–s overlapping.



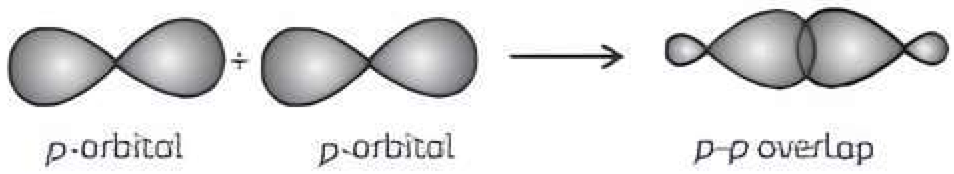
*s–s orbital overlapping*

**s–p Overlapping:** When one atom's half-filled s-orbital overlaps with another atom's half-filled p-orbital this type of overlapping is called s–p overlapping.



*s–p orbital overlapping*

**p–p Overlapping:** When two half-filled p– orbitals of two atoms overlap it is called p – p overlapping.



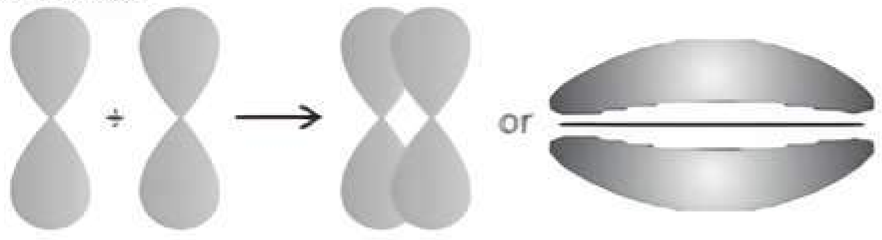
*p–p orbital overlapping*

**Important**

➥ *If x-axis is chosen as the internuclear axis and can overlap with s-orbital whereas no overlapping can take place between the orbitals, i.e., there is zero overlap.*

**(2) Pi-bond (π)**

When the atomic orbitals overlap in such a way that their axes remain parallel to each other and perpendicular to the internuclear axis. This is called the pi-bond. The orbitals formed by sidewise overlap of atomic orbitals consist of charged electron clouds which are in saucer type above and below the plane of atoms.



*p – p Orbital sidewise overlapping*

## Strength of Sigma and Pi-Bonds

The strength of a bond generally depends on the extent of overlapping of atomic orbitals. The sigma bond is stronger than the pi-bond as the sigma bonds overlap to a greater extent than the pi-bond which overlaps to a smaller extent.

In the multiple bond formation, one bond should be a sigma and the other should be a pi-bond.

**Example 3.4:** **Distinguish between a sigma and a pi-bond.** **[NCERT]**

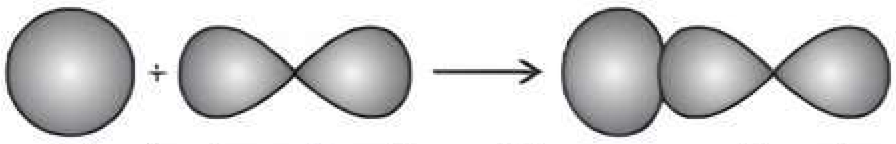
**Ans.**

| Sigma Bond | Pi-Bond |
|---|---|
| This bond is formed by the axial overlap of atomic orbitals. | This bond is formed by the side-wise overlap of atomic orbitals. |
| The bond is stronger. | The bond is weaker. |
| The molecular orbital is symmetrical about the internuclear axis and consists of a single charged cloud. | The molecular orbital is discontinuous and consists of two charged clouds above and below the plane of atoms. |
| This bond can be formed by overlap of s – s, s–p or p–p orbitals | It involves overlap of p-orbitals only. |

**Example 3.5:** **Case Based:**

*Valance bond theory was first proposed by Heitler and London and this theory was later developed by Pauling and others. The basic idea of VBT is from atomic orbital, electronic configurations, atomic orbitals overlap and variation and superposition principles. Depending on the types of overlaps different types of bonds are determined.*

**(A) The given diagram corresponds to which type of overlapping:**



**(a) d – d overlapping (b) s – p overlapping**
**(c) p – p overlapping (d) s – s overlapping**

**(B) The pi-bonding is formed by:**

**(a) Side-wise overlap**
**(b) Head-on overlap**
**(c) No overlap**
**(d) Two s-orbitals overlap**

**(C) What is s – s overlapping?**

**(D) Why $N_2$ molecule is less strong than the $H_2$ molecule?**

**(E) Assertion (A): The head-on overlap gives a sigma bond.**

**Reason (R): $O_2$ molecules have only a sigma bond.**

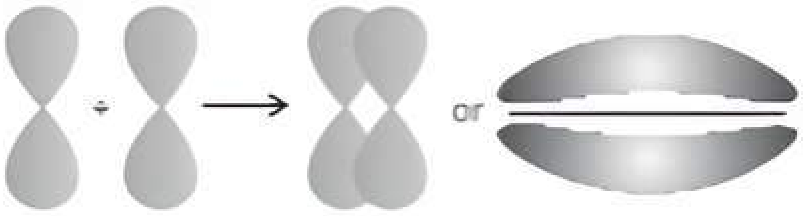
**(a) Both (A) and (R) are true and (R) is the correct explanation of (A).**
**(b) Both (A) and (R) are true but (R) is not the correct explanation of (A).**
**(c) (A) is true but (R) is false.**
**(d) (A) is false but (R) is true.**

**Ans.** **(A)** *(b) s–p overlapping*

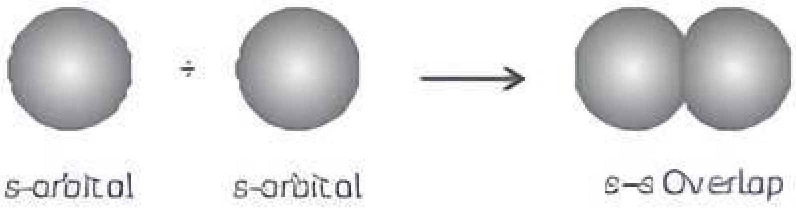
**Explanation:** Based on the given diagram, the spherical-shaped orbital is s-orbital and the dumbbell-shaped orbital is p-orbital. So, it is s–p overlapping. The d–d overlapping will appear as an interaction between two clover leaf-shaped-like orbitals. So it is the incorrect one. The *p–p* overlapping of orbitals will appear as an interaction between two dumbbell-shaped orbitals. So, this is also incorrect. The *s–s* overlapping will appear as an interaction between two spherical-shaped orbitals. But the diagram given above is not like the one. So this is also an incorrect answer.

**(B)** *(a) Side-wise overlap*

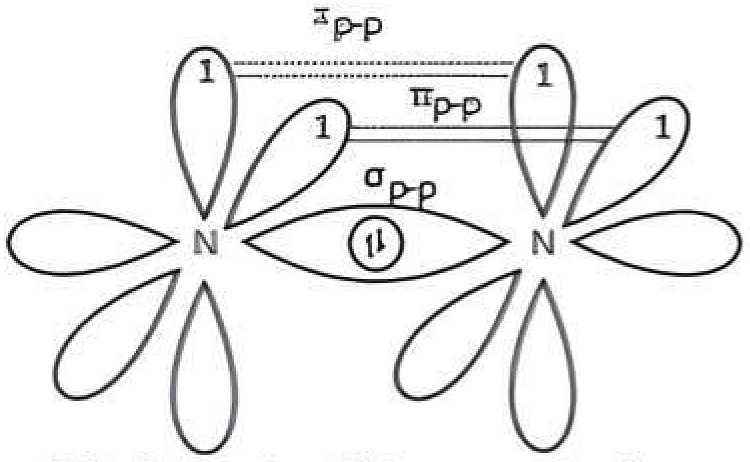
**Explanation:** The pi-bond is formed by the sidewise overlap of atomic orbitals. The head-on overlap will occur for the formation of sigma bonds. This option is the incorrect one.



**(C)** When two half-filled s-orbitals overlap along the internuclear axis it is called s–s overlapping.



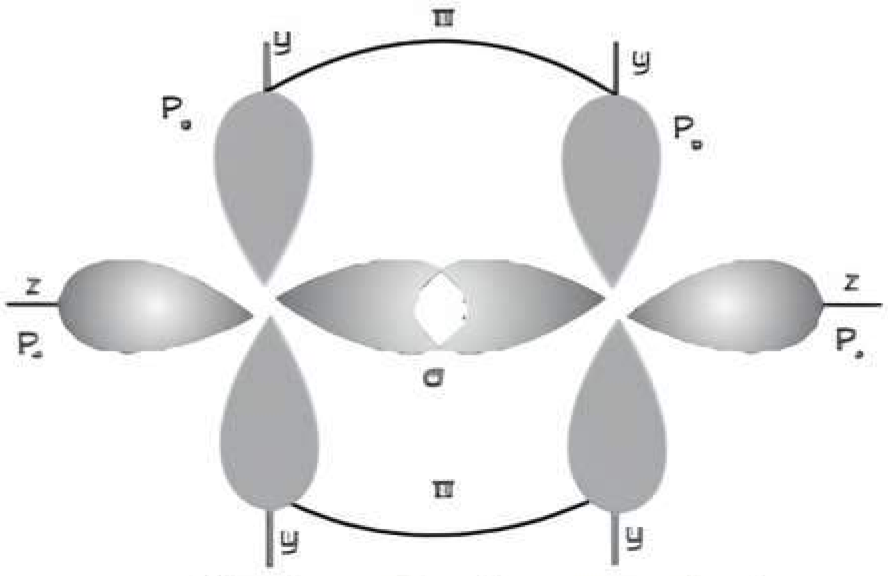
**(D)** The $H_2$ molecule is stronger than the $N_2$ molecule. As the hydrogen molecules are formed by the head-on overlap of orbitals which have a greater extent of overlap tend to be stronger. The nitrogen molecules formed by sideways overlap tend to be weaker.



*Sidewise overlap of nitrogen molecule*

**(E)** *(c) (A) is true but (R) is false.*

**Explanation:** The head-on overlap gives the sigma bond whereas the side-wise overlap gives the pi-bond. The oxygen molecule has one sigma and one pi-bond. Thus reason is incorrect.



*Sidewise overlap of oxygen molecule*

## OBJECTIVE Type Questions

[ 1 mark ]

### Multiple Choice Questions

1. **The $BH_3$ molecule belongs to which type:**

| | |
|---|---|
| (a) $AB_4$ | (b) $AB_3$ |
| (c) $AB_2$ | (d) $AB_3E$ |

**Ans.** *(b) $AB_3$*

**Explanation:** The $BH_3$ belongs to $AB_3$ type as it has three H atoms with a central atom and has no lone pair of electrons.

The molecule $AB_3E$ contains a lone pair of electrons but the given $BH_3$ molecule doesn't have a lone pair of electrons. So, this is incorrect. $AB_3$ means the molecules should have one central atom which has the valency of four, but the given molecule has a valency of three so this is incorrect. $AB_4$ means the central atom with two valencies, but the given molecule has a valency of three, so, this is also incorrect.

**Related Theory**

→ *The AB represents the molecules that are made of different types of atoms that have a central atom whose valency is satisfied by other types of atoms which are bond pairs and E represents the lone pair of electrons that will not take place in bonding.*

2. **The $BeCl_2$ molecules exist in which of the geometry?**

| | |
|---|---|
| (a) Tetrahedral | (b) Trigonal planar |
| (c) Linear | (d) Octahedral |

**[NCERT Exemplar]**

**Ans.** *(c) Linear*

**Explanation:** In $BeCl_2$ *Be*. is the central atom with Cl attached on both sides forming linear geometry of about bond angle of 180°. Tetrahedral geometry will not be possible as central atom's valency should be 4, but here only 2 valency is there. So, this is incorrect. In Trigonal planar, the central atom's valency should be 3 So, this geometry is also incorrect. In Octahedral geometry, the central atom's valency should be 6. So this geometry is also incorrect.

**3. Identify the molecule having side-wise overlapping of atomic orbitals.**

(a) $CH_4$ (b) $CO_2$

(c) $NH_3$ (d) $H_2O$

**Ans.** *(b) $CO_2$*

**Explanation:** The covalent bond formed by the side-wise overlap of atomic orbitals is called as pi-bond. Pi-bond is found in $CO_2$.

**4. Match the following:**

| Molecule type | Ideal shape |
|---|---|
| (A) $AB_2$ | (i) Tetrahedral |
| (B) $AB_3$ | (ii) Pentagonal bipyramidal |
| (C) $AB_4$ | (iii) Octahedral |
| (D) $AB_5$ | (iv) Linear |
| (E) $AB_6$ | (v) Trigonal Planar |

(a) (A)-(iv), (B)-(v), (C)-(i), (D)-(ii), (E)-(iii)

(b) (A)-(v), (B)-(ii), (C)-(iii), (D)-(i), (E)-(iv)

(c) (A)-(iv), (B)-(v), (C)-(i), (D)-(iii), (E)-(ii)

(d) (A)-(i), (B)-(iv), (C)-(ii), (D)-(iii), (E)-(v)

**Ans.** *(a) (A)-(iv), (B)-(v), (C)-(i), (D)-(ii), (E)-(iii)*

**Explanation:**

| Molecule type | Ideal shape | Example |
|---|---|---|
| $AB_2$ | Linear | $BeCl_2$ |
| $AB_3$ | Trigonal planar | $BF_3$ |
| $AB_4$ | Tetrahedral | $CH_4$ |
| $AB_5$ | Pentagonal bipyramidal | $PCl_5$ |
| $AB_6$ | Octahedral | $SF_6$ |

**5. The electronic configuration of the excited carbon atom is:**

(a) [He] $2s^1, 2p_x^1, 2p_y^1, 2p_z^1$

(b) [He] $2s^2\ 2p^2$

(c) [He] $1s^2$

(d) [He] $2s^2\ 2p^5$

**Ans.** *(a) [He] $2s^1, 2p_x^1, 2p_y^1, 2p_z^1$*

**Explanation:** In the excited state, one of the electrons from the $2s^2$ jumped into $2p_z$.

**6. Which of the following species have the same shape?**

(I) $BeCl_2$ (II) $BF_3$

(III) $CH_4$ (IV) $NH_4^+$

**Select the correct option:**

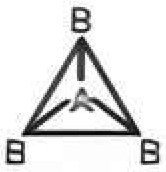
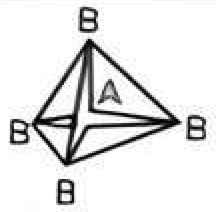
(a) (I) and (II) (b) (I) and (III)

(c) (II) and (III) (d) (III) and (IV)

**[NCERT Exemplar]**

**Ans.** *(d) (III) and (IV)*

**Explanation:** Both the molecules, $CH_4$ and $NH_4^+$ have the same tetrahedral geometry. $BeCl_2$ have linear geometry, whereas $BF_3$ have trigonal planar geometry.

| Molecule geometry | Hybridisation | Example |
|---|---|---|
| B — A — B<br>Linear | $sp$ | $BeCl_2$, $HgCl_2$ |
| <br>Trigonal planar ($AB_3$) | $sp^2$ | $BF_3$ |
| <br>Trigonal ($AB_4$) | $sp^3$ | $CH_4$, $NH_4^+$ |

**7. The number of bond pairs and lone pairs present in the $SF_4$ molecule are:**

(a) 4 and 1 (b) 2 and 1

(c) 2 and 3 (d) 4 and 2

**Ans.** *(a) 4 and 1*

**Explanation:** Total no. of electrons = 6 + 4 = 10

No. of bond pair electrons = 8

No. of lone pair electrons = 10–8 = 2

∴ No. of lone pair = 2/2=1

Thus, the $SF_4$ molecule has four bond pairs and one lone pair.

**Caution**

➥ *The students may confuse between electrons and an electron pair. An electron pair means it has two electrons and an electron mean a single electron. A single electron pair means that it contains 2 electrons.*

**8. There are zero overlaps between:**

(a) s and $p_x$ orbital (b) s and $p_z$ orbital

(c) $p_z$ and $p_z$ orbital (d) s and s orbital

**[Diksha]**

**Ans.** *(a) s and $p_x$ orbital*

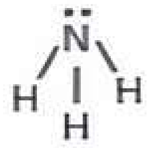
**Explanation:** The s and $p_x$ have zero overlapping as they have different orientations and different energies. The $p_z$ and $p_z$ and s and s-orbital have symmetrical orientation and it will give negative or positive overlap. The symmetrical orientation would not give zero overlaps.

**9.** The number of lone pairs present in the $NH_3$ molecule is:

(a) 2 (b) 1
(c) 3 (d) 0

**Ans.** *(b) 1*

**Explanation:** The $NH_3$ molecule contains 3 bond pairs and 1 lone pair.



*$NH_3$ molecule structure*

## Assertion-Reason (A-R)

In questions no. (10–13) a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choice.

(a) Both (A) and (R) are true and (R) is the correct explanation of (A).
(b) Both (A) and (R) are true but R is not the correct explanation of (A).
(c) (A) is true but (R) is false.
(d) (A) is false but (R) is true.

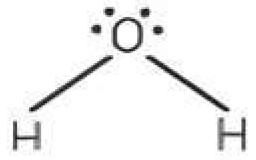
**10.** **Assertion (A):** The $H_2O$ molecule has a bent shape.

**Reason (R):** The water molecule has lone pairs which make the geometry deviate from the tetrahedral geometry.

[NCERT exampler]

**Ans.** *(a) Both (A) and (R) are true and (R) is the correct explanation of (A).*

**Explanation:** The $H_2O$ molecule has four electron pairs, out of which two are bond pairs and two are lone pairs which make the molecule deviate from the original structure.



*Water molecule bent structure*

**Related Theory**

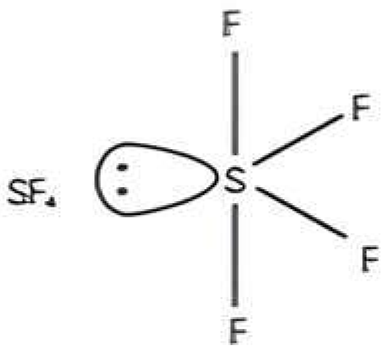
- *The repulsive interaction of electron pairs decreases in the given order:*
*Lone pair-lone pair > Lone pair-bond pair > Bond pair-bond pair.*

**11.** **Assertion (A):** According to VBT, the shape of a molecule depends on the number of valence electrons present around the central atom.

**Reason (R):** The shape of $SF_4$ is a see-saw due to the extra valence electron pair present on the central atom Sulphur.

**Ans.** *(a) Both (A) and (R) are true and (R) is the correct explanation of (A).*

**Explanation:** Both statements are correct. The sulphur atom has six valence electrons, out of which four electrons are satisfied by fluorine molecules and a pair remain as lone pair of electrons.



*See-saw shape of $SF_4$ structure.*

**12.** **Assertion (A):** The isolated hydrogen atom is less stable than a hydrogen molecule.

**Reason (R):** The two hydrogen atoms are combined to get stability.

**Ans.** *(a) Both (A) and (R) are true and (R) is the correct explanation of (A).*

**Explanation:** All the molecules tend to attain stability. During the formation of hydrogen molecules, the two atoms of hydrogen combine to form molecules with a release of energy which reflects that isolated atoms of hydrogen are less stable than a hydrogen molecule.

$$H_{(g)} + H_{(g)} \rightarrow H_{2(g)} + 435.8 \text{ kJmol}^{-1}$$

**13.** **Assertion (A):** The sigma bond is stronger than the pi-bond.

**Reason (R):** This is due to the greater extent of overlapping of pi bonds.

**Ans.** *(c) (A) is true but (R) is false.*

**Explanation:** The sigma bond is stronger due to the greater extent of overlapping between the atomic orbital. This reason is incorrect because the greater extent of overlapping is seen in the sigma bond, not in the pi-bond.

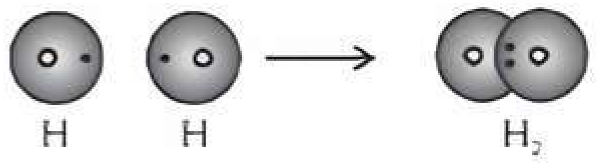
## CASE BASED Questions (CBQs)

[ **4** & **5** marks ]

Read the following passages and answer the questions that follow:

**14.** *The simplest case to consider overlapping is the hydrogen molecule, $H_2$. When we say that the* *two electrons from each of the hydrogen atoms are shared to form a covalent bond between the two atoms, what we mean in valence bond theory terms is that the two spherical 1s orbitals overlap, allowing the two electrons to form a pair within the two overlapping orbitals. In simple terms, we can say that both electrons now spend more time between the two nuclei and thus hold the atoms together. As we will see, the situation is not quite so simple as that, because the electron pair must still obey quantum mechanics - that is, the two electrons must now occupy a shared orbital space. This will be the essential principle of valence bond theory.*

*How far apart are the two nuclei? That is a very important issue to consider. If they are too far apart, their respective 1s orbitals cannot overlap, and thus no covalent bond can form - they are still just two separate hydrogen atoms. As they move closer and closer together, orbital overlap begins to occur, and a bond begins to form. This lowers the potential energy of the system, as new, attractive positive-negative electrostatic interactions become possible between the nucleus of one atom and the electron of the second. However, something else is happening at the same time: as the atoms get closer, the repulsive positive-positive interaction between the two nuclei also begins to increase.*



**(A) Which type of overlapping is there in $Cl_2$ molecule?**

**(a) s – s overlapping**
**(b) s – p overlapping**
**(c) p – p overlapping**
**(d) d – d overlapping**

**(B) Which type of overlapping is stronger?**

**(a) d – d overlapping**
**(b) p – p overlapping**
**(c) s – s overlapping**
**(d) s – p overlapping**

**(C) The bond in $F_2$ molecule is ______ than $O_2$ molecule**

**(a) weaker (b) stronger**
**(c) little weaker (d) little stronger**

**(D) There are zero overlaps between**

**(a) s and $p_x$ orbitals (b) s and $p_z$ orbitals**
**(c) $p_z$ and $p_x$ orbitals (d) s and s orbitals**

**(E) Choose the incorrect statement about overlapping:**

**(a) In $H_2O$ molecule there are one sigma and one pi-bond.**

**(b) Ammonia molecules contain three sigma bonds.**

**(c) In HCl, molecule has a sigma bond.**

**(d) Oxygen molecules contain one sigma bond and one pi-bond.**

**Ans.** (A) *(c) p – p overlapping*

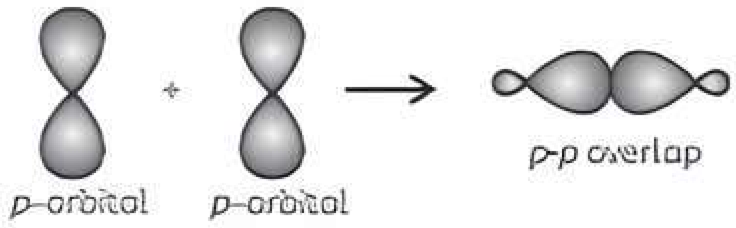
**Explanation:** The $Cl_2$ molecule exhibit *p–p* overlapping. The electronic configuration of two chlorine atoms is $[Ne]3s^2 3p^5$. The *p*–orbital is the orbital containing valence electrons which only involves in bonding by overlapping of the two atomic orbitals (i.e. *p*–orbital) of chlorine.

(B) *(c) s – s overlapping*

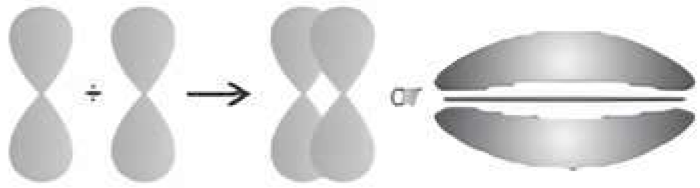
**Explanation:** The s–s *overlapping* is stronger than other overlaps. This is due to the similar size of *s–orbital* (Spherical) and they are having high electronegativity so the overlap between them is stronger.

(C) *(b) stronger*

**Explanation:** The bond in $F_2$ molecule is stronger than $O_2$. Because the Fluorine molecule involves the head-on overlap which forms a sigma bond and the oxygen molecule involves side-wise overlap to form a pi-bond. The sigma bond is the stronger bond than the pi-bond due to the effective overlapping of the sigma bond.



*p-p orbital overlapping forming sigma bond in fluorine molecule*



*π bond formation*

(D) *(a) s and $p_x$ orbitals*

**Explanation:** s and $p_z$ orbitals show zero overlaps.

(E) *(a) In $H_2O$ molecule there are one sigma and one pi-bond.*

**Explanation:** In water molecules, there are two sigma bonds where the oxygen is attached to the two hydrogen atoms. So, this statement is incorrect one. There is no pi-bond in the water molecule.

**15.** *In 1956, British scientists R.J. Gillespie and R.S. Nyholm recognized that the current model for explaining bond angles did not work well. The theory at that time relied on hybrid orbitals to explain all aspects of bonding. The problem was that this theory gave an incorrect prediction of bond angles for many compounds. They developed a new approach* *based on earlier work by other scientists that incorporated a consideration of electron pairs in predicting three-dimensional structures.*

*The valence shell is the outermost electron-occupied shell of an atom. The valence shell holds the electrons that are involved in bonding and are the electrons shown in a Lewis structure. The acronym VSEPR stands for the valence-shell electron pair repulsion model. The model states that electron pairs will repel each other such that the shape of the molecule will adjust, so that the valence electron-pairs stay as far apart from one another as possible. Molecules can be systematically classified according to the number of bonding pairs of electrons, as well as the number of nonbonding, or lone pairs, around the central atom. For the purposes of the VSEPR model, a double or triple bond is no different in terms of repulsion than a single bond.*

*A few molecules are given below, answer the following questions based on these molecules.*

*$CH_4$, $PCl_5$, $SF_6$, $H_2O$ and $XeF_4$*

**(A) Identify the molecules which don't have a lone pair of electrons and give the number of bond pairs present in them.**

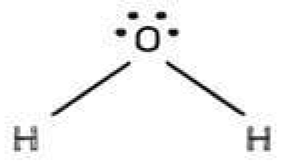
**(B) Identify the molecule having four bond pairs and determine its geometry.**

**(C) Find the molecules which are having lone pairs of electrons and draw their structures.**

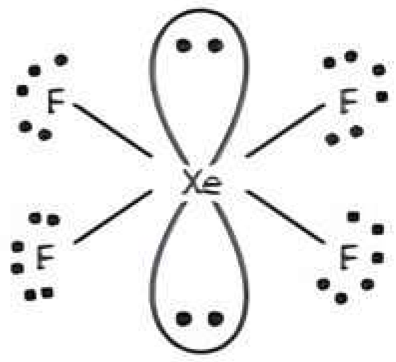
**Ans.** (A) The molecules which do not have lone pairs of electrons are $SF_6$, $CH_4$ & $PCl_5$. The valence electrons present in the central atom S is 6 that are satisfied by the 6 fluorine atoms, so no lone pairs are there. The valence electrons in carbon are 4 which are all satisfied by 4–H atoms so no more lone pair is there and the valence electrons present in the P are 5 which are all satisfied by 5 – Cl atoms. So, it also does not have a lone pair of electrons.

(B) The $CH_4$ (methane) molecule is having four bond pairs where the four valencies of carbon are satisfied by four hydrogen atoms. So, four bond pairs are present. The methane molecule is in a tetrahedral geometry.

(C) Among the given options $H_2O$ and $XeF_4$ have both lone pairs and bond pairs. Both the molecules have 2 lone pairs on central atom.



Structure of $H_2O$ molecule



Structure of $XeF_4$

**Caution**

*The students may get confused whether the lone pair present on the adjacent atoms should be considered or not. The lone pair that is present on the central atom is only considered and, not on the adjacent atom. Here, in the $XeF_4$ the lone pair on the central atom xenon is only considered and not present on fluorine atoms.*

## VERY SHORT ANSWER Type Questions (VSA)

[ 1 mark ]

**16. Explain why $PCl_5$ molecule has trigonal bipyramidal geometry whereas $IF_5$ have a square pyramidal shape? [NCERT Exemplar]**

**Ans.** In $PCl_5$ molecule, the central phosphorus atom has 5 valence electrons which mean 5 bond pairs correspond to the trigonal bipyramidal shape and $IF_5$ molecule having 7 valence electrons around the central atom iodine, the 5 valencies are satisfied by five fluorine atoms and the remaining one lone pair which makes the distortion in structure to form a square pyramidal shape.

**17. Why does $SF_6$ adopt octahedral geometry and $SF_4$ adopt a see-saw shape?**

**[NCERT Exemplar]**

**Ans.** The $SF_6$ molecule has sulphur as the central atom has 6 valence electrons which are all satisfied by 6 fluorine atoms, but in the case of $SF_4$ and only 4 valancies are satisfied by F-atoms and the other two electrons remain as a lone pair of electrons. So, $SF_6$ has an octahedral shape while $SF_4$ has distortion in structure which is a see-saw shape.

**18. Explain the effect of overlapping in the bond strength.**

**Ans.** The strength of a bond generally depends on the extent of overlapping of atomic orbitals. The sigma bond is stronger than the pi-bond as the sigma bonds overlap to a greater extent than the pi-bond which overlaps to a smaller extent.

**19. $HgCl_2$ belongs to which type $AB_2$ or $AB_3$? Explain.**

**Ans.** The $HgCl_2$ molecule represents $AB_2$ type, as it is not having any lone pair, it only has 2 bond pairs.

$$Cl—Hg—Cl$$

*$HgCl_2$ structure*

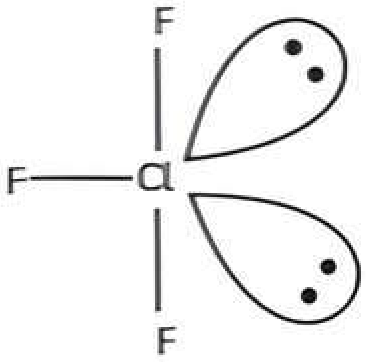
# SHORT ANSWER Type-I Questions (SA-I)

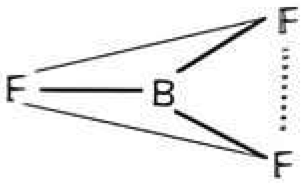
[ **2** marks ]

**20.** $ClF_3$ is T shaped but $BF_3$ is planar. Explain. [Delhi Gov. QB 2022]

**Ans.** $ClF_3$ has $sp^3d$-hybridisation with two lone pairs of electrons on Cl. The expected shape of $ClF_3$ should be trigonal bipyramidal but due to the presence of two lone pairs of electrons, the shape is T-shaped.

$BF_3$ molecule has a planar structure as it is $sp^2$ hybridised (it has 3 bond pairs and no lone pair).





**21.** What type of attractive and repulsive force arises when two atoms come closer to form a molecule?

**Ans.** The attractive forces can occur between

(1) The nucleus of an atom and its electron $N_A - e_A$ and $N_B - e_B$.

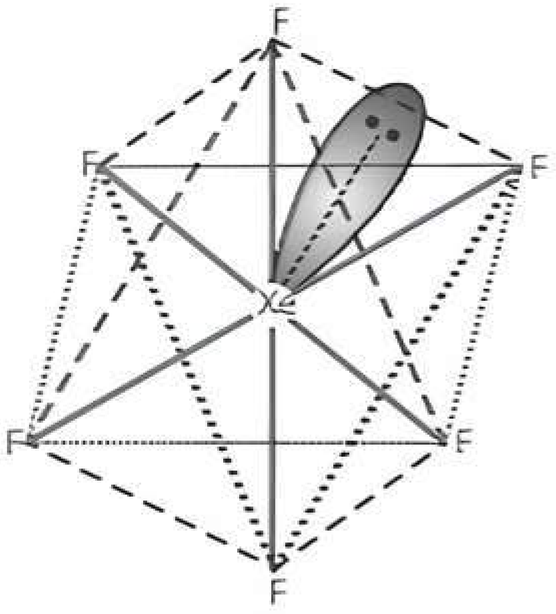
(2) The nucleus of an atom and the other atom's electron. $N_A - e_B$, $N_B - e_A$.

The repulsive force may occur between

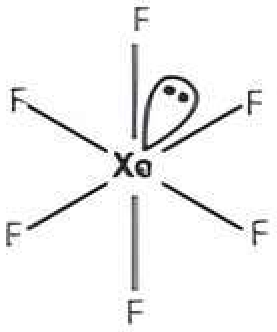
(1) The electron belongs to two atoms $e_A - e_B$.

(2) The nuclei belong to two atoms $N_A - N_B$.

**22.** Draw the structure of $XeF_6$ and the name of the geometry.



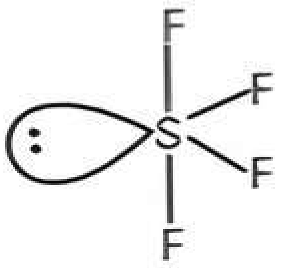
$XeF_6$ geometry



Distorted octahedral

**23.** Draw the structure of molecule having 4 bond pairs and 1 lone pair.

**Ans.** The molecule which has 4 bond pairs and one lone pair is $SF_4$ where the sulphur (central atom) is having 6 valence electrons. The 4 valence electrons are satisfied by 4 fluorine atoms and 2 electrons remain as a lone pair electron.



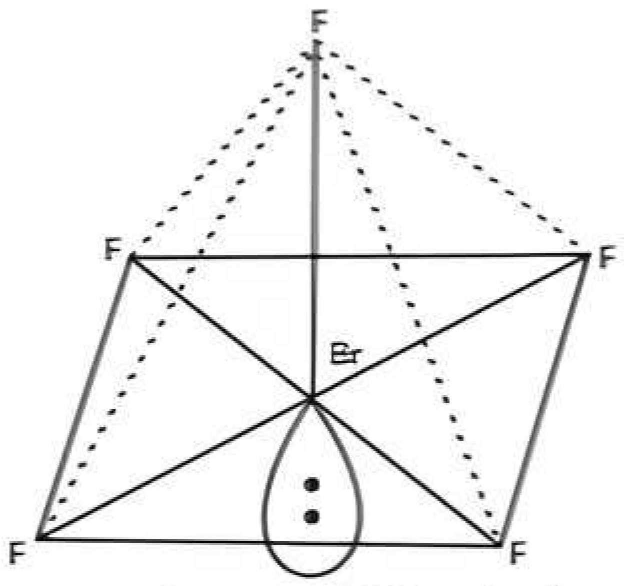
See-saw shape

# SHORT ANSWER Type-II Questions (SA-II)

[ **3** marks ]

**24.** Explain the shape of $BrF_5$. [NCERT Exemplar]

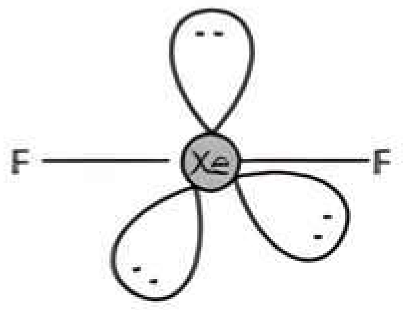
**Ans.** The bromine atom has an electronic configuration of $1s^2$, $2s^2 2p^6$, $3s^2 3p^6 3d^{10}$, $4s^2 4p^5$. To get pentavalency, two of the p-orbitals are unpaired and electrons are shifted to 4d-orbitals. In this excited state molecule occurs octahedral structure. The five valencies of bromine are satisfied by five fluorine atoms forming a sigma bond and a remaining lone pair occupies the position and makes the structure distorted from octahedral to square pyramidal shape.



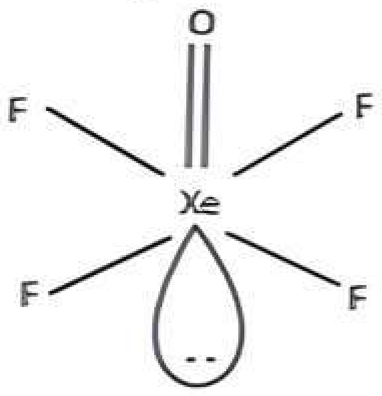
Structure of $BrF_5$ molecule

**25.** **Draw the shape of the following molecules according to VSEPR theory; $XeO_3$, $XeF_2$, $XeOF_4$.**

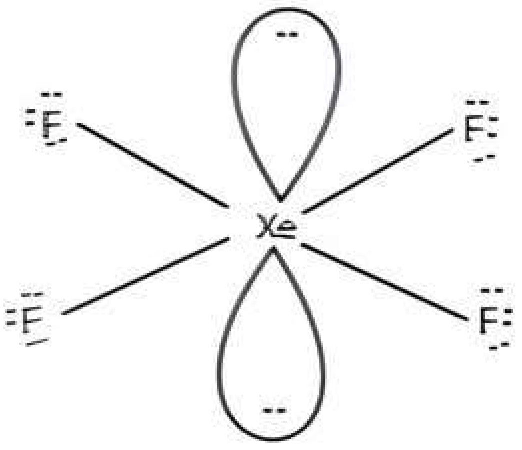
**Ans.** In $XeF_2$, Xe is $sp^3d$-hybridised but its shape is linear due to the involvement of VSEPR theory i.e. due to the presence of three lone pairs of electrons. Thus, geometry of $XeF_2$ is distorted from trigonal bipyramidal to linear.



In $XeOF_4$, Xe undergoes $sp^3d^2$ hybridisation but its shape is square pyramidal due to the involvement of VSEPR theory (i.e. due to the presence of one lone pair of electrons, geometry of $XeOF_4$ is distorted from octahedral to square pyramidal).



In $XeF_4$, Xe is $sp^3d^2$-hybridised but its shape is square planar due to the involvement of VSEPR theory. (i.e. due to the presence of one lone pair of electrons, geometry of $XeF_4$ is distorted from octahedral to square planar).



**26.** **(A) Why is free rotation about a $\pi$-bond not possible?**

**(B) $H_2$ exists whereas $He_2$ does not exist. Explain on the basis of valence bond theory.**

**(C) Which one has greater directional orientation, *p*-orbital or *sp*-orbital, and why?** **[Diksha]**

**Ans.** (A) As the overlapping vanishes and the bond breaks the free rotation is not possible.

(B) According to the valence bond theory half or singly filled orbitals overlap each other to form a covalent bond.

In case of $H_2$ the two atoms are half-filled with one electron overlap whereas in case of $He_2$, the two He atoms have fully-filled orbitals which cannot overlap to form a bond.

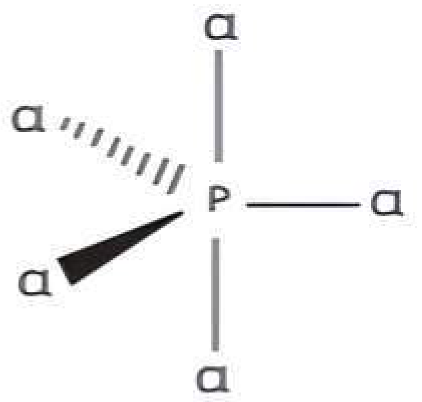
(C) The *p*-orbital lobes are equal on both the sides. So, electron density is equal on both the sides.

**Shape of *sp*-orbitals:**

*sp*-orbitals have one lobe larger than the other and most of the *sp*-probability density is on the bigger lobe. This makes the *sp* orbital more directional.

**27.** **How many bond pairs and lone pairs are present in the $PCl_5$ molecule and draw its geometry?** **[NCERT Exemplar]**

**Ans.** The phosphorus pentachloride has five bond pairs and zero lone pairs. The central atom is phosphorus of valence five which are all satisfied by five Cl so no more lone pair of electrons. It has pentagonal bipyramidal geometry.



*$PCl_5$ molecule*

## LONG ANSWER Type Questions (LA)

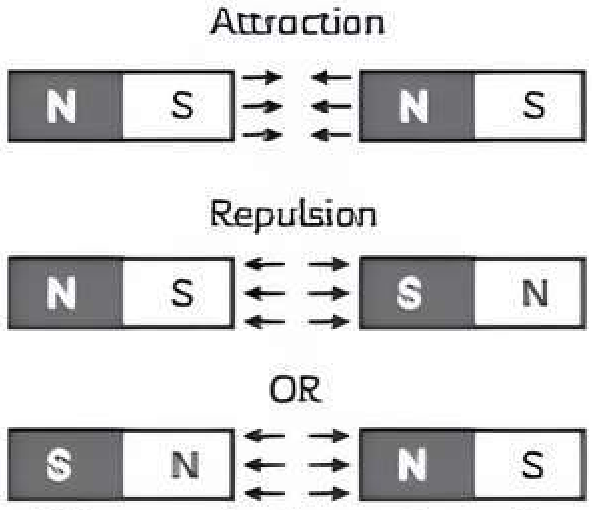
[ **4** & **5** marks ]

**28.** **Explain the VBT theory.**

**Ans.** (1) The basic idea of VBT comes from atomic orbital, electronic configurations, atomic orbital's overlap and variation and superposition principles. To understand this, we can consider a simple example.

(2) Consider the two hydrogen atoms A and B. The nucleus of these atoms can be represented by $N_A$ & $N_B$ and the electrons in these atoms can be written as $e_A$ & $e_B$. When the two atoms are far apart there will be no interaction, when they are at a nearer

distance then there will be some attractive and repulsive interaction between them.



*A real-life example of attraction and repulsion between bar magnets.*

The attractive forces can occur between

The nucleus of an atom and its electron $N_A - e_A$ and $N_B - e_B$.

The nucleus of an atom and the other atom's electron. $N_A - e_B$, $N_B - e_A$.

The repulsive force may occur between

The electron belongs to two atoms $e_A - e_B$.

The nuclei belong to two atoms $N_A - N_B$.

(3) The attractive force brings the two atoms close together, and repulsive force pushes them for away.

(4) The experimental results show that the magnitude is greater for attractive forces than repulsive forces. So, when the atoms approach closer the potential energy decreases.

(5) At a particular time, the resultant attractive force balances the repulsive force and the system requires minimal energy. At this point, the hydrogen atoms get bonded together to form a stable molecule having a bond length of 74 pm.

(6) During the formation of hydrogen molecules, the energy gets released which reflects that isolated atoms of hydrogen are less stable than a hydrogen molecule. The energy released during the formation of a molecule is called bond enthalpy. The energy required to dissociate one mole of the $H_2$ molecule is

$$H_{2(g)} + 435.8 \text{ kJmol}^{-1} \rightarrow H_{(g)} + H_{(g)}$$

**29. Write the postulates of VSEPR theory.** **[NCERT Exemplar]**

**Ans.** (1) The molecules are made up of different types of atoms, one of which is a central atom.

(2) The shape of a molecule depends upon the number of electron pairs in the valence shell which includes (bonded or non-bonded electrons) around the central atom.

(3) The electron pairs repel each other since the electron clouds are negatively charged.

(4) The electron pair tends to be in the maximum distance so that the repulsion between the electrons will be minimum.

(5) The valence shell is taken as a sphere where the electron pairs are localising on the spherical surface which will be at a maximum distance.

(6) The single or double or triple electron pairs are counted as an only one electron pair.

(7) The VSEPR theory is also applicable to molecules that have two or more resonance structures.

(8) The repulsive interaction of electron pairs decreases in the given order:
lone pair-lone pair > lone pair-bond pair > bond pair-bond pair.

**30. What is refined VBT theory?**

**Ans.** (1) Nyholm and Gillespie refined the VSEPR theory and explained the important difference between the lone pairs and bonding pairs. The lone pairs are localised on the central atom and bond pairs are shared between two atoms.

(2) The lone pair occupies more space than bonding pairs of electrons. So, there is a greater repulsion between lone pairs as compared to bonding pairs of electrons.

(3) This repulsion affects the idealised shapes of the molecules and deviation in bond angles occurs.

(4) The VSEPR theory divides molecules into two types:

(i) The molecules in which the central atom has no lone pair of electrons.

(ii) The molecules in which the central atom has one or more lone pairs of electrons.

| Molecule type | Ideal shape | Example |
|---|---|---|
| $AB_2$ | Linear | $BeCl_2$ |
| $AB_3$ | Trigonal planar | $BF_3$ |
| $AB_4$ | Tetrahedral | $CH_4$ |
| $AB_5$ | Pentagonal bipyramidal | $PCl_5$ |
| $AB_6$ | Octahedral | $SF_6$ |

(5) The VSEPR theory predicts the geometry of the various molecules, especially element's geometry. It is also useful in determining the geometry of the molecules even if their different possible structures have smaller energy differences. The VSEPR theory is a theoretical one that cannot explain certain molecular shapes.

(6) When lone pairs of an electron are present then the ideal shape of the molecules gets distorted.

# HYBRIDISATION AND MOLECULAR ORBITAL THEORY

# 4

## TOPIC 1

## HYBRIDISATION

The phenomenon of intermixing of pure atomic orbitals to produce a new set of equivalent orbitals (known as hybrid orbitals) is called *hybridisation*. During this process, only valence shell orbitals having equal energy and shape take part.

### Postulates

(1) The total number of hybrid orbitals formed is equal to the total number of atomic orbitals used in the bonding.

(2) The bond formed by hybrid orbitals is stronger than atomic orbitals.

(3) Both half-filled and fully-filled orbitals can take part in hybridisation.

(4) The hybrid orbitals arrange themselves in space in such a way so that there are minimum repulsions between electron pairs and thus get a stable arrangement. Therefore, the type of hybridisation indicates the geometry of the molecules.

### Types of Hybridisation

#### *sp* Hybridisation

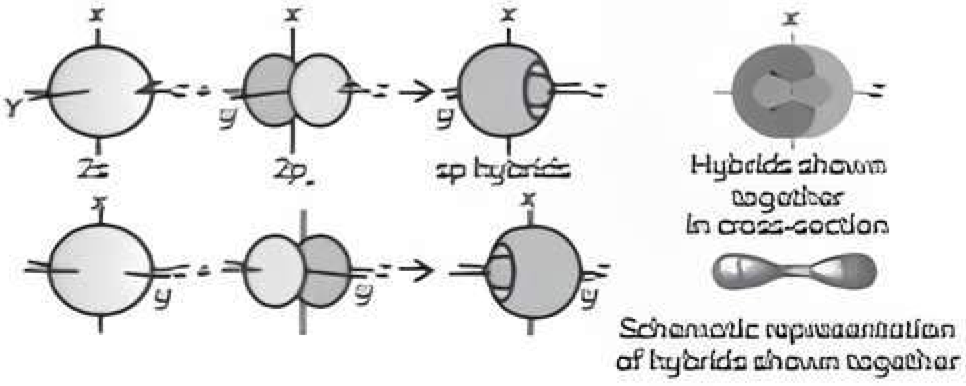
In this type of hybridisation, one s and one *p* orbital intermix with each other to give two equivalent *sp* hybrid orbitals. Along with s, $P_z$ orbital is preferred in *sp* hybridisation because these orbitals have the same orientation in space. This hybridisation is also known as diagonal hybridisation.

In *sp* hybridisation,

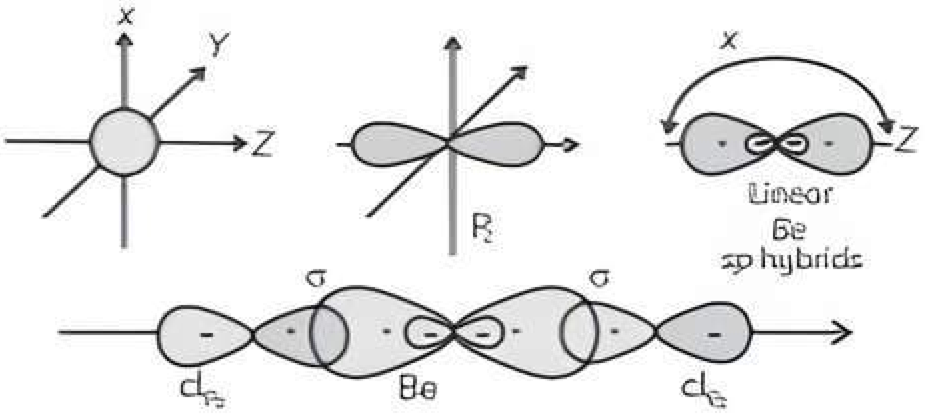
$$\% \text{ s-character: } \frac{1}{2} \times 100 = 50\%$$

$$\% \text{ p-character: } \frac{1}{2} \times 100 = 50\%$$

The two *sp* hybrids point in the opposite direction along the *z*-axis with projecting positive lobes and very small negative lobes, which provides more effective overlapping resulting in the formation of stronger bonds.



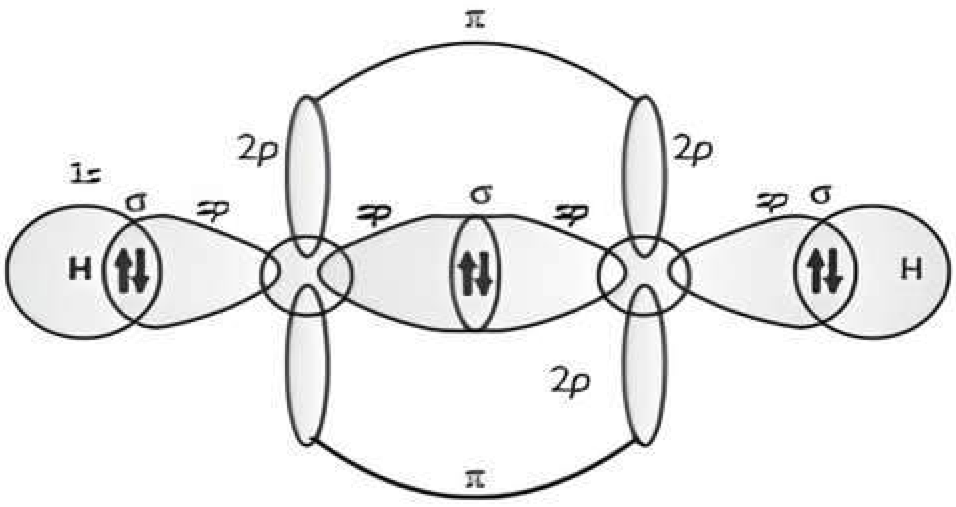
Molecules with *sp* hybridized central atoms possess linear geometry. For example, $BeCl_2$.



**Example 4.1:** Explain *sp* hybridisation in $C_2H_2$.

[NCERT]

**Ans.**



As we can see, acetylene molecules form three sigma bonds. Two of them are with 1s orbital of hydrogen with 2*p* orbital of carbon and other is between 2*p*–2*p* orbital of carbon atoms. Other two pi-bonds are result of sideways overlapping of 2*p* carbon orbitals.

So, each carbon has two sigma bonds and zero lone pairs.

Now    Hybrid orbitals = total number of sigma bonds + total number of lone pair

Thus, hybrid orbitals: (2 + 0) = 2

Hybridisation = *sp*.

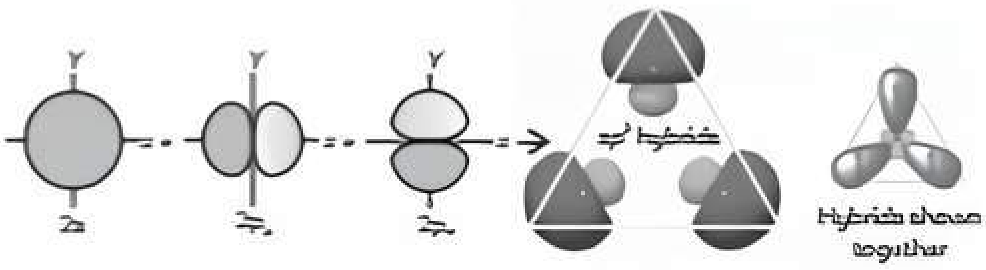
## $sp^2$ Hybridisation

In this type of hybridisation, one *s* and two *p* orbitals intermix with each other to give three equivalent $sp^2$ hybrid orbitals.

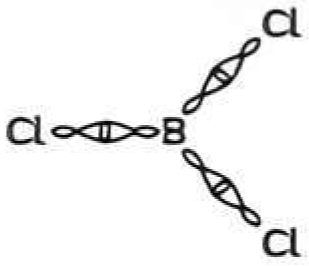
In $sp^2$ hybridisation,

% *s*-character: $\frac{1}{2} \times 100 = 33.33\%$

% *p*-character: $\frac{2}{3} \times 100 = 66.67\%$



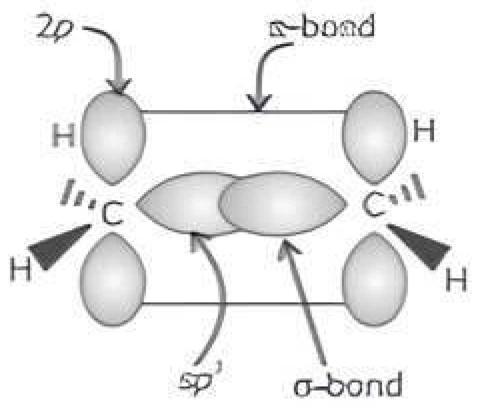
Molecules with $sp^2$ hybridised central atoms possess trigonal planar geometry. For example, $BCl_3$

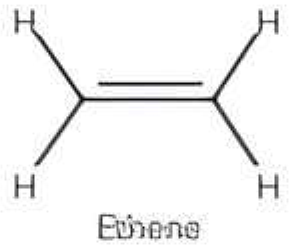


**Example 4.2:** Explain $sp^2$ hybridisation in $C_2H_4$.

[NCERT]

**Ans.**





Ethene

There are total of five sigma bonds in ethene molecule. Four σ-bonds are formed by overlap between 1s orbital of hydrogen with 2*p* orbital of carbon and π-bond is between 2*p*-2*p* orbital of carbon atoms. A pi-bond is result of side-wise overlapping of carbon orbitals.

So, each carbon has three sigma bonds and zero lone pairs.

Now,    Hybrid orbitals = total number of sigma bonds + total number of lone pairs

Thus, hybrid orbitals: (3 + 0) = 3

Hybridisation: $sp^2$.

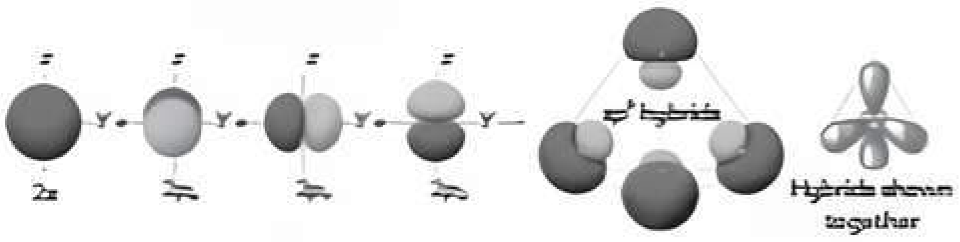
## $sp^3$ Hybridisation

In this type of hybridisation, one *s* and three *p* orbitals intermix with each other to give four equivalent $sp^3$ hybrid orbitals.

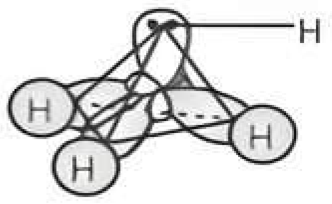
In $sp^3$ hybridisation,

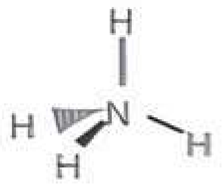
% s-character: $\frac{1}{4} \times 100 = 25\%$

% *p*-character: $\frac{3}{4} \times 100 = 75\%$



Molecules with $sp^3$ hybridized central atoms possess tetrahedral geometry. For example, $CH_4$.

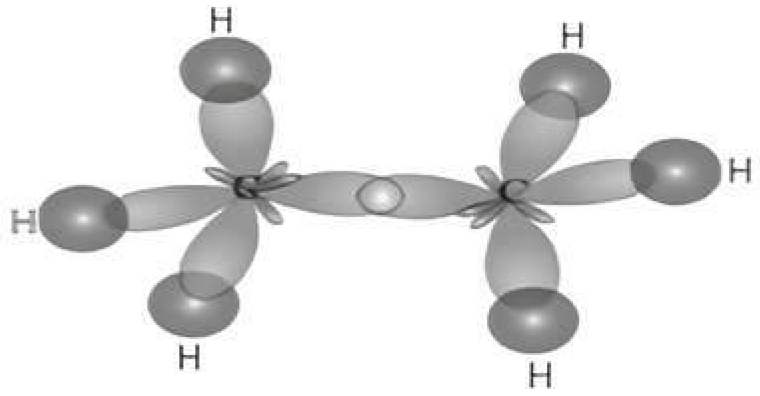




**Example 4.3:** Explain $sp^3$ hybridisation in : $C_2H_6$

[NCERT]

**Ans.**



In ethane molecules, there are 7 sigma bonds. Six of them are formed with 1*s* orbital of a hydrogen atom with 2*p* orbital of carbon and seventh σ-bond is formed by overlapping of 2*p*-2*p* orbital of carbon atoms. So, each carbon has four sigma bonds and zero lone pairs.

Now,    Thus, hybrid orbitals = (4 + 0) = 4

Hybridisation = $sp^3$

### ⚠ Caution

➥ *While calculating the number of hybrid orbitals, students should always keep in mind to count the number of lone pairs.*

For example: In the case of $H_2O$.

Total bond pair: 2 and number of hybrid orbitals: 4 (this is because it has two lone pairs)

So, both bond pairs and lone pairs contribute to hybridisation.

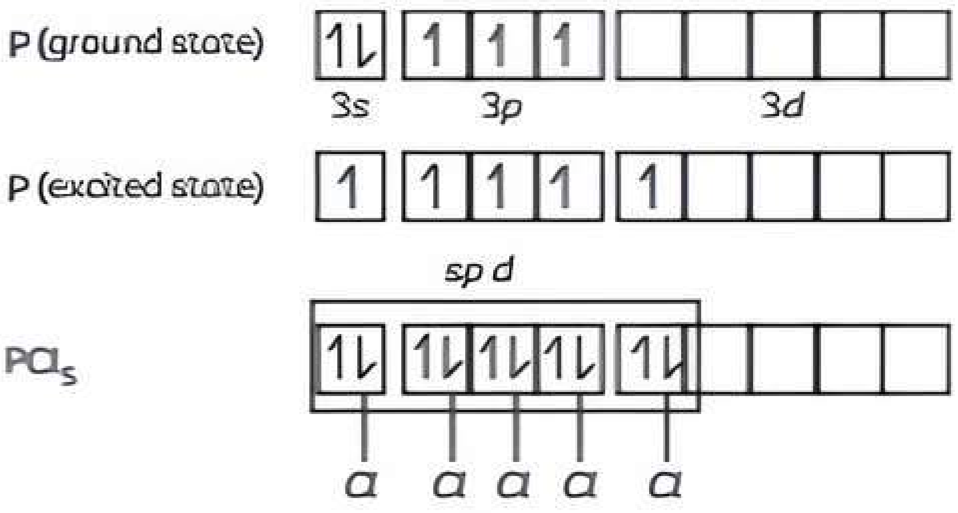
## $sp^3d$ Hybridisation

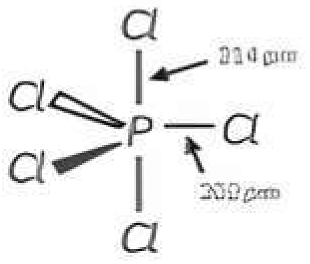
Hybridisation involving *d* orbitals: $sp^3d$

Here, one s, three p and one d orbitals intermix with each other to give five equivalent $sp^3d$ hybrid orbitals.

This hybridisation posseses trigonal bipyramidal geometry where there are 3 equatorial bonds (bond angle = 120°) and 2 axial bonds(bond angle = 90°).

It has been found that the axial bond experiences greater repulsions than equatorial bonds. Thus axial bonds are slightly longer and hence slightly weaker than the equatorial bonds. For eg: $PCl_5$



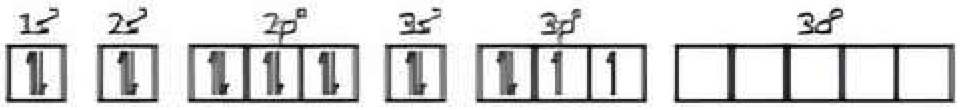


### $sp^3d^2$ Hybridisation

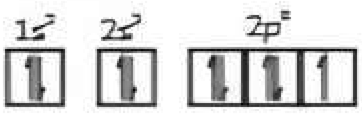
Here one s, three p and two d-orbitals intermix with each other to give six equivalent $sp^3d^2$ hybrid orbitals.

This hybridisation posseses a regular octahedral geometry where all the bonds are equal in length. For eg. $SF_6$

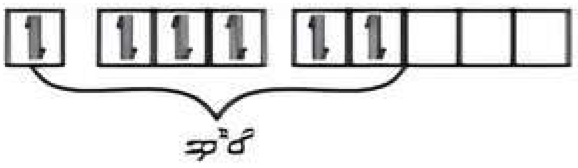
Sulphur (in ground state)

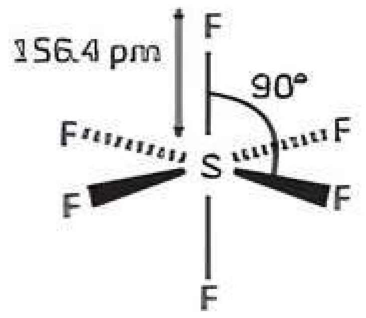


Fluorine –



After hybridisation, valence shell electronic configuration of Sulphur





**Important**

- Number of Hybrid orbitals (H) = $\frac{1}{2}$ (No. of valence electrons in valence shell of central atom the atom+ No. of monovalent atoms surrounding - Charge on cation + Charge on anion)

| Value of H | Type of hybridisation |
|---|---|
| 2 | $sp$ |
| 3 | $sp^2$ |
| 4 | $sp^3$ |
| 5 | $sp^3d$ |
| 6 | $sp^3d^2$ |
| 7 | $sp^3d^3$ |

Table: Electronic configuration, molecular shapes, their Hybridisation and bond angles.

| Total number of electron clouds | Electronic shape | Hybridisation | Bond angles | Bonding $e^-$ clouds | Lone pair | Molecular shapes |
|---|---|---|---|---|---|---|
| 2 | Linear | $sp$ | 180° | 2 | 0 | Linear |
| 3 | Trigonal Planar | $sp^2$ | 120° (slightly less with lone pairs) | 3 | 0 | Trigonal Planar |
| | | | | 2 | 1 | Bent |
| 4 | Tetrahedral | $sp^3$ | 109.5° (slightly less with lone pairs) | 4 | 0 | Tetrahedral |
| | | | | 3 | 1 | Trigonal Pyramidal |
| | | | | 2 | 2 | Bent |

| Total number of electron clouds | Electronic shape | Hybridisation | Bond angles | Bonding $e^-$ clouds | Lone pair | Molecular shapes |
|---|---|---|---|---|---|---|
| 5 | Trigonal bipyramidal | $sp^3d$ | 90° (axial)<br>120° (equatorial) | 5 | 0 | Trigonal bipyramidal |
| | | | <90° (axial)<br><120° (equatorial) | 4 | 1 | See-saw |
| | | | <90° (axial) | 3 | 2 | T-shaped |
| | | | 180° | 2 | 3 | Linear |
| 6 | Octahedral | $sp^3d^2$ | 90° (slightly less with lone pairs) | 6 | 0 | Octahedral |
| | | | | 5 | 1 | Square pyramidal |
| | | | | 4 | 2 | Square planar |

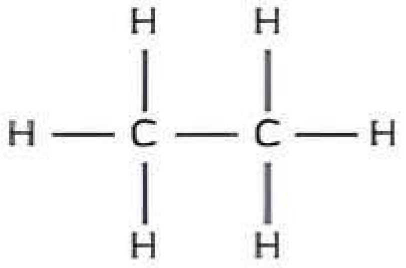
**Example 4.4: Which hybrid orbitals are used by carbon atoms in the following molecules?**

**(A)** $CH_3-CH_3$ **(B)** $CH_3-CH=CH_2$

**(C)** $CH_3-CH_2-OH$ **(D)** $CH_3-CHO$

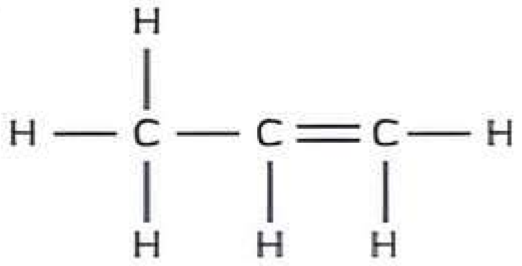
**(E)** $CH_3-COOH$

**Ans. (A)**



Each carbon atom has four sigma bonds and zero lone pairs. So, the total number of hybrid orbitals is 4. Thus, both carbon atoms are $sp^3$ hybridized.

**(B)**

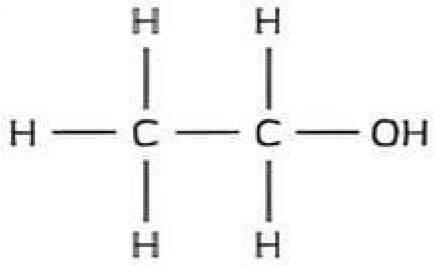


First carbon atom has four hybrid orbitals $= sp^3$ hybridisation

Second carbon atom has three hybrid orbitals $= sp^2$ hybridisation

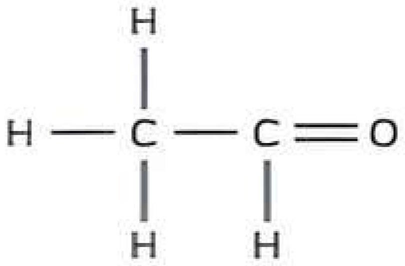
Third carbon atom has three hybrid orbitals $= sp^2$ hybridisation.

**(C)**



Both carbon atoms have four hybrid orbitals $= sp^3$ hybridized.

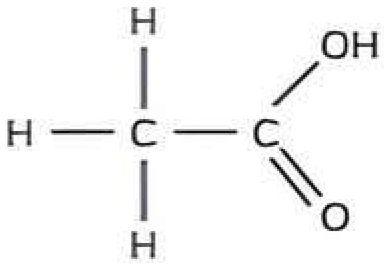
**(D)**



First carbon atom has four hybrid orbitals $= sp^3$ hybridisation

Second carbon atom has three hybrid orbitals $= sp^2$ hybridisation.

**(E)**



First carbon atom has four hybrid orbitals $= sp^3$ hybridisation

Second carbon atom has three hybrid orbitals $= sp^2$ hybridisation.

**Example 4.5: Case Based:**

*Phosphorus pentachloride is a greenish-yellow crystalline solid having an irritating odour. It is prepared by passing an excess of dry chlorine into liquid phosphorus trichloride. It is used as a chlorinating agent and as a catalyst in many organic reactions. In the pharmaceutical industry, it is used in the manufacture of penicillin and various other important drugs. $PCl_5$ is a reactive chemical. Its direct exposure can cause weakness and headaches. Also, it may damage the vital organs of our body like the liver and kidney.*

(A) The hybridisation of $PCl_5$ molecule is:

(a) $sp^3$ (b) $sp^3d^2$

(c) $sp^3d$ (d) $sp^2$

(B) $Cl - P - Cl$ bond angles in $PCl_5$ molecule are:

(a) 120° and 90° (b) 60° and 90°

(c) 60° and 120° (d) 120° and 30°

(C) Draw the structure of $PCl_5$.

(D) Why are the axial bonds longer as compared to equatorial bonds in $PCl_5$ structure?

(E) Assertion (A): All bond lengths are equal in $PCl_3$ but not in $PCl_5$.

Reason (R): Hybrid state of central atom is different in both cases.

(a) Both (A) and (R) are true and (R) is the correct explanation of (A).

(b) Both (A) and (R) are true but (R) is not the correct explanation of (A).

(c) (A) is true but (R) is false.

(d) (A) is false but (R) is true.

**Ans.** (A) *(c) $sp^3d$*

**Explanation:** Number of Hybrid orbitals

(H) = $\frac{1}{2}$ (No. of valence electrons in valence shell of central atom + No. of monovalent atoms surrounding – Charge on cation + Charge on anion)

For $PCl_5$

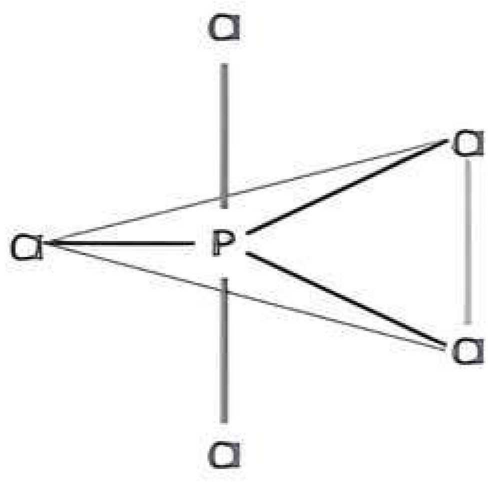
$$(H) = \frac{1}{2}(5 + 5) = 5$$

since the value of H = 5 so the hybridisation would be $sp^3d$.

(B) *(a) 120° and 90°*

**Explanation:** $PCl_5$ molecule has trigonal pyramidal geometry. The equatorial bonds in the $PCl_5$ molecule form 120° angle bonds and the axial bonds in the $PCl_5$ molecule form 90° degree angle bonds.

(C)



(D) In $PCl_5$ there are two axial and three equatorial bonds. As the axial bond pairs suffer more repulsion as compared to equatorial bond pairs, the axial bonds are longer as compared to equatorial bonds.

(E) *(b) Both (A) and (R) are true but (R) is not the correct explanation of (A).*

**Explanation:** For $PCl_3$

$$(H) = \frac{1}{2}(5 + 3)$$
$$= 4$$

Since H = 4, the hybridisation will be $sp^3$.

Here, all the bond lengths are equal.

For $PCl_5$

$$(H) = \frac{1}{2}(5 + 5) = 5$$

since the value of H = 5 so the hybridisation would be $sp^3d$.

In $PCl_5$ as the axial bond pairs suffer more repulsion as compared to equatorial bond pairs, the axial bonds are longer as compared to equatorial bonds.

**Example 4.6:** Case Based:

*The elements of Group 18 will have been called inert gases. The name noble gases imply that they tend to be unreactive, in the same way that the noble metals are often reluctant to react and are the least reactive metals. The gases He, Ne, Ar, Kr, and Xe all occur in the atmosphere. The elements are all colourless, odourless monoatomic gases. The chemistry of Xe is quite interesting. Xe reacts directly only with $F_2$. However, oxygen compounds can be obtained from the fluorides. The compounds $XeF_2$, $XeF_4$ and $XeF_6$ are all white solids. The lower fluorides form higher fluorides when heated with $F_2$ under pressure. The fluorides are all extremely strong oxidizing and fluorinating agents.*

(A) What is the hybridisation of $XeF_2$?

(a) $sp^2$ (b) $sp^3d$

(c) $sp^3d^2$ (d) None of these

(B) What is the geometry of $XeO_3$?

(a) Tetrahedral

(b) Square planar

(c) Trigonal pyramidal

(d) None of these

(C) Draw the structure of $XeF_6$.

(D) The structure of $XeF_2$ is linear whereas $XeF_4$ is square planar. Give reason.

(E) Assertion (A): The structure of $PCl_5$ and $XeF_2$ is trigonal bipyramidal.

Reson(R): They both have $sp^3d$ hybridisation.

(a) Both (A) and (R) are true and (R) is the correct explanation of (A).

(b) Both (A) and (R) are true but (R) is not the correct explanation of (A).

(c) (A) is true but (R) is false.

(d) (A) is false but (R) is true.

**Ans. (A)** *(b) $sp^3d$*

**Explanation:** For $XeF_2$

$$(H) = \frac{1}{2}(8 + 2)$$
$$= 5$$

Hybridisation: $sp^3d$

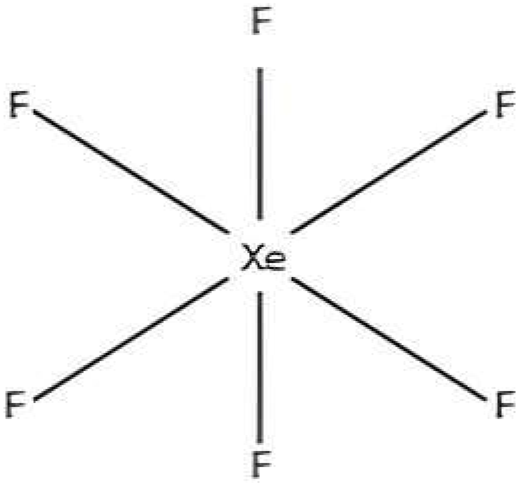
**(B)** *(c) Trigonal pyramidal*

**Explanation:** $(H) = \dfrac{(8 + 0)}{2} = 4$

Hybridisation: $sp^3$

Geometry: Trigonal pyramidal

**(C)**

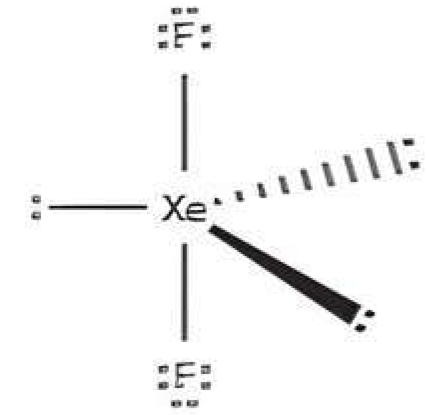


**(D)** For $XeF_2$

$$(H) = \frac{1}{2}(8 + 2)$$
$$= 5$$

Hybridisation: $sp^3d$

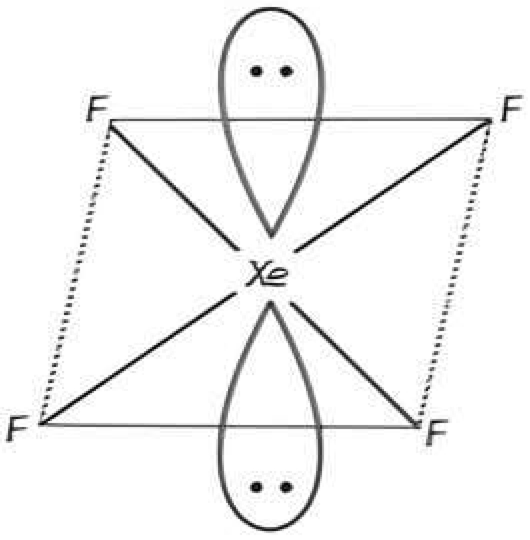
Since the hybridisation is 5 it should have a trigonal bipyramidal structure. But because of the presence of 3 lone pairs occupying the equatorial positions, its geometry would be linear.



For $XeF_4$

$$(H) = \frac{1}{2}(8 + 4)$$
$$= 6$$

The shape of $XeF_4$ is octahedral but because of the presence of 2 lone pairs at the perpendicular axis, its geometry would be square planar.



**(E)** *(d) (A) is false but (R) is true.*

**Caution**

- *Although both have $sp^3d$ hybridisation but their geometries are different. This is because of presence of three lone pairs on $XeF_2$ giving it a linear geometry whereas no lone pair is present on $PCl_5$ giving it a trigonal bipyramidal structure.*

## TOPIC 2

## MOLECULAR ORBITAL THEORY

F. Hund and R.S. Mulliken developed the Molecular Orbital Theory (MOT) in 1932. This theory explains the characteristics of molecules like relative bond strength, magnetic nature, etc.

### Postulates of MOT

(1) In MOT all electrons (including inner electrons) are involved in bond formation.

(2) Atomic orbitals of comparable energies and proper symmetry combine together to give molecular orbitals.

(3) Molecular orbitals are formed by the LCAO (Linear Combination of atomic orbitals) method and once molecular orbitals are formed atomic orbitals lose their identity.

(4) Molecular orbitals are defined as 3D space in a molecule at which the probability of finding an electron is maximum.

(5) The number of molecular orbitals obtained is always equal to the number of combining atomic orbitals. There are two types of molecular orbitals bonding molecular orbitals and non-bonding molecular orbitals.

(6) Bonding orbitals are formed by constructive interference and non-bonding orbitals are formed by destructive interference.

(7) Bonding molecular orbitals have lower energy than atomic orbitals and anti-bonding orbitals have higher energy than atomic orbitals.

(8) The electron probability distribution around a group of nuclei in a molecule is given by a molecular orbital.

(9) All rules of electron filling like the Aufbau principle, the pauli exclusion principle and the Hund's rule are valid in filling of electrons in the molecular orbital.

## Formation of Molecular Orbitals: Linear Combination of Atomic Orbitals (LCAO)

According to this method, the molecular orbitals are formed by the linear combination of atomic orbitals that takes place by addition and by subtraction of wave functions of individual atomic orbital.

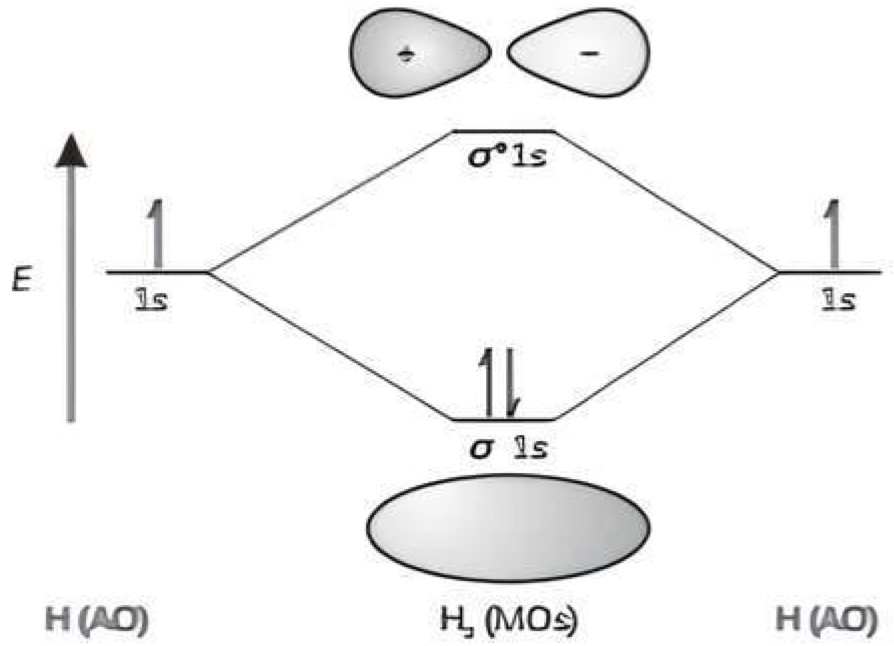
Let us consider the hydrogen molecule consisting of two atoms $H_A$ and $H_B$. Each hydrogen atom in the ground state has one electron in 1s orbital. The atomic orbitals of these atoms may be represented by the wave functions $\psi_A$ and $\psi_B$. The molecular orbital is given as:

$$\psi_{MO} = \psi_A + \psi_B$$

There are two molecular orbitals σ and σ* which are formed as:

$\sigma = \psi_A + \psi_B$ (bonding molecular orbital)

$\sigma^* = \psi_A - \psi_B$ (anti-bonding molecular orbital)



The electron density in a bonding molecular orbital is located between the nuclei of the bonded atoms because of which the repulsion between the nuclei is very less. Thus the energy of the bonding orbital has been lowered than the parent orbitals. While in the case of an antibonding molecular orbital, most of the electron density is located away from the space between the nuclei. Infact, there is a nodal plane (on which the electron density is zero) between the nuclei and hence the repulsion between the nuclei is high, so the energy of the antibonding orbital is raised above the energy of the parent atomic orbitals. The energy of the antibonding orbital is raised above the energy of the parent atomic orbitals.

## Conditions for Linear Combination of Atomic Orbitals

The conditions that are required for the linear combination of atomic orbitals are as follows:

### Same Energy of Combining Orbitals

Atomic orbitals combining to form molecular orbitals should have comparable energy. This means that the 2*p* orbital of an atom can combine with another 2*p* orbital of another atom but 1s and 2*p* cannot combine together as they have appreciable energy differences.

### Same Symmetry about Molecular Axis

The combining atoms should have the same symmetry around the molecular axis for proper combination, otherwise, the electron density will be sparse. For e.g., all the sub-orbitals of 2*p* have the same energy but still, $2p_z$ orbital of an atom can only combine with a $2p_z$ orbital of another atom but cannot combine with $2p_x$ and $2p_y$ orbital as they have a different axis of symmetry. In general, the *z*-axis is considered as the molecular axis of symmetry.

### Proper Overlap between Atomic Orbitals

The two atomic orbitals will combine to form a molecular orbital if the overlap is proper. The greater the extent of overlap of orbitals, the greater will be the nuclear density between the nuclei of the two atoms.

The condition can be understood by two simple requirements. For the formation of a proper molecular orbital, proper energy and orientation are required. For proper energy, the two atomic orbitals should have the same energy and for the proper orientation, the atomic orbitals should have proper overlap and the same molecular axis of symmetry.

## Types of Molecular Orbitals

Molecular orbitals of diatomic molecules are designated as σ (sigma), π (pi), δ (delta), etc. In this nomenclature, the sigma (σ) molecular orbitals are symmetrical around the bond axis while pi (π) molecular orbitals are not symmetrical.

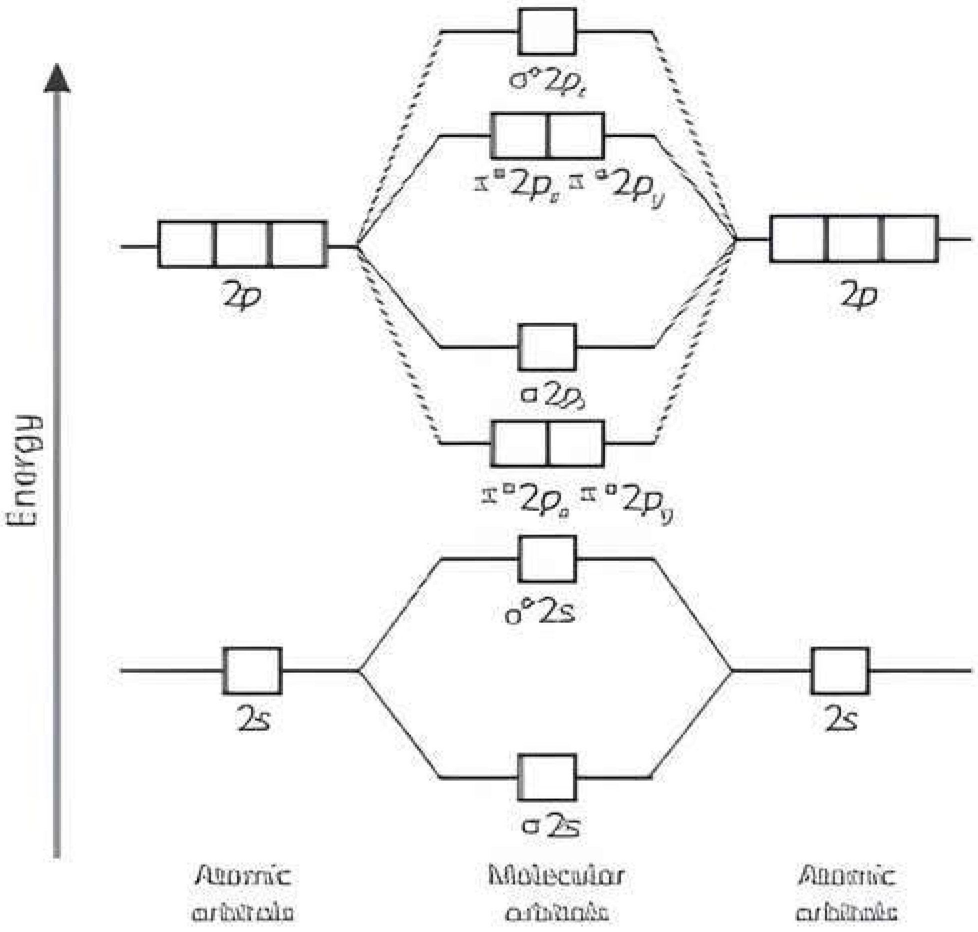
Sigma (σ) molecular orbital: These orbitals are formed when the atomic orbitals overlap along the internuclear axis. These atomic orbitals are formed by the combination of s atomic orbitals or $p_z$ atomic orbitals or s with $p_z$ atomic orbitals. Such molecular orbitals are of the σ type and are designated as σ s and σ*s.

pi (π) molecular orbital: These orbitals are formed when the atomic orbital overlap sideways. These atomic orbitals are formed by the combination of $p_x$ and $p_y$ orbitals. Such molecular orbitals are labelled as π and π*.

## Molecular Orbital Diagram

**CASE 1:** If no. of electrons are less than 14.

MO diagram for period 2 elements $Li_2$ to $N_2$



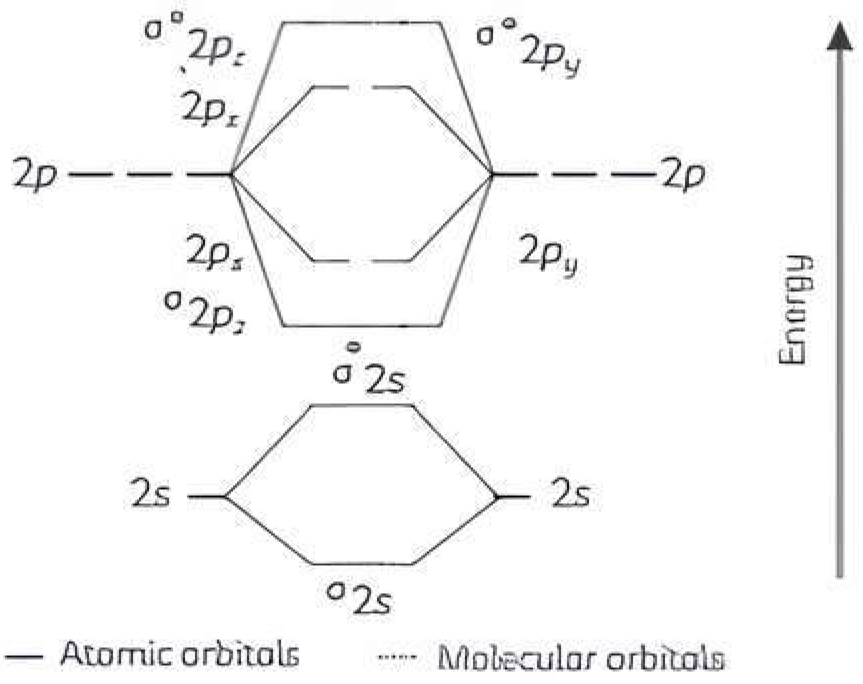
e.g. $Li_2$, $Be_2$, $B_2$, $C_2$, $N_2$ etc.

So, order of energy is:

$$\sigma_{1s} < \sigma^*_{1s} < \sigma_{2s} < \sigma^*_{2s} < (\pi 2p_x = \pi 2p_y) < \sigma 2p_z < (\pi^* 2p_x = \pi^* 2p_y) < \sigma^* 2p_z$$

**CASE 2:** If no. of electrons are greater than 14.

MO diagram for period 2 elements from O to Ne



Eg. $O_2$, $F_2$ etc.

So, order of energy is:

$$\sigma_{1s} < \sigma^*_{1s} < \sigma_{2s} < \sigma^*_{2s} < \sigma 2p_z < (\pi 2p_x = \pi 2p_y) < (\pi^* 2p_x = \pi^* 2p_y) < \sigma^* 2p_z$$

**Important**

➥ *In the first case energy of $\sigma_{2p_z}$ is greater than $(\pi_{2p_x} = \pi_{2p_y})$ because of s-p mixing. And in the second case there is an energy difference between s and p-orbitals so, mixing of s-p orbitals does not take place that's why energy of $(\pi_{2p_x} = \pi_{2p_y})$ is greater than $\sigma_{2p_z}$*

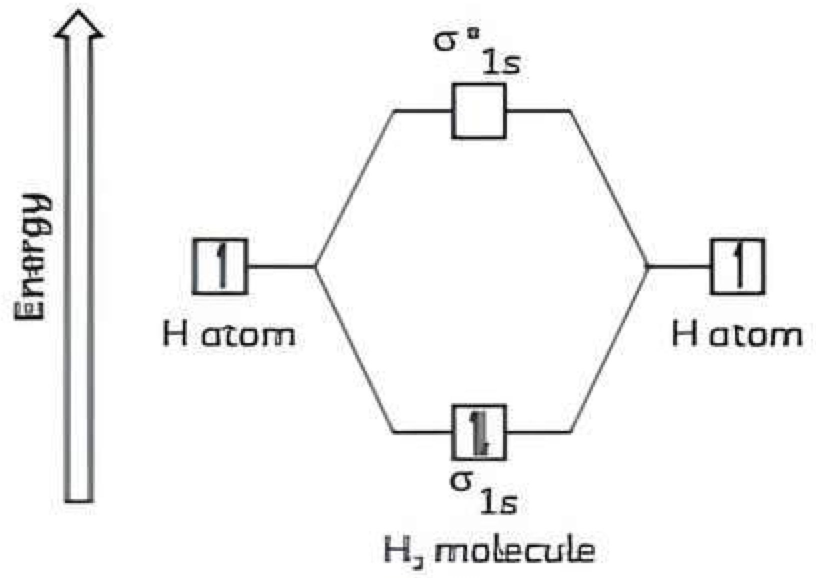
## Bonding in Some Homonuclear Diatomic Molecules

Here the term homonuclear means that there is only one type of nucleus, i.e., one element is present and diatomic means that the molecule is composed of two atoms.

Examples of some such molecules are given below:

### Hydrogen Molecule

It is formed when two hydrogen atoms combine together. The number of electrons in one H atom = 1



∴ Number of electrons in $H_2$ molecule = 1 + 1 = 2

MO configuration of $H_2 = \sigma 1s^2$

Here $N_b = 2$ and $N_a = 0$

$$\text{The bond order} = \frac{N_b - N_a}{2} = \frac{2-0}{2} = 1$$

Bond order 1 means that the two hydrogen atoms are bonded together by a single covalent bond. The bond dissociation energy of hydrogen molecule has been found to be 438 kJ $mol^{-1}$ and bond length equal to 74pm. Since, there is no unpaired electron in the hydrogen molecule, so it is diamagnetic. Its molecular orbital energy level diagram is given above.

**Important**

➥ *Positive value of bond order indicates that the $H_2$ molecule is stable. Bond order value of 1 means that the two H atoms are connected by a single bond.*

**The electronic configuration, bond order and magnetic properties of some diatomic molecules are given in the following table:**

Table: Electronic configuration, bond order and magnetic properties of some important molecules.

| S. No. | Molecule/ Ion | No. of Electrons | Electronic configuration | Bond order | Magnetic property |
|---|---|---|---|---|---|
| 1. | $H_2$ | 2 | $\sigma 1s^2$ | $\frac{1}{2}(2-0)=1$ | Stable and Diamagnetic |
| 2. | $He_2$ | 4 | $\sigma 1s^2 . \overset{\bullet}{\sigma} 1s^2$ | $\frac{1}{2}(2-2)=0$ | Stable and Does not exist |
| 3. | $Li_2$ | 6 | $\sigma 1s^2 . \overset{\bullet}{\sigma} 1s^2 . \sigma 2s^2$ | $\frac{1}{2}(4-2)=1$ | Stable and Diamagnetic |
| 4. | $Be_2$ | 8 | $\sigma 1s^2 . \overset{\bullet}{\sigma} 1s^2 . \sigma 2s^2 . \overset{\bullet}{\sigma} 2s^2$ | $\frac{1}{2}(4-4)=0$ | Stable and Does not exist |
| 5. | $B_2$ | 10 | $\sigma 1s^2 . \overset{\bullet}{\sigma} 1s^2 . \sigma 2s^2 . \overset{\bullet}{\sigma} 2s^2 .$<br>$\pi 2p_x{}^1 \approx \pi 2p_y{}^1$ | $\frac{1}{2}(6-4)=1$ | Stable and Paramagnetic |
| 6. | $C_2$ | 12 | $\sigma 1s^2 . \overset{\bullet}{\sigma} 1s^2 . \sigma 2s^2 . \overset{\bullet}{\sigma} 2s^2 .$<br>$\pi 2p_x^2 \approx \pi 2p_y{}^2$ | $\frac{1}{2}(8-4)=2$ | Stable and Diamagnetic |
| 7. | $N_2$ | 14 | $\sigma 1s^2 . \overset{\bullet}{\sigma} 1s^2 . \sigma 2s^2 . \overset{\bullet}{\sigma} 2s^2 .$<br>$\pi 2p_x{}^2 \approx \pi 2p_y{}^2 . \sigma 2p_z{}^2$ | $\frac{1}{2}(10-4)=3$ | Stable and Diamagnetic |
| 8. | $O_2$ | 16 | $\sigma 1s^2 . \overset{\bullet}{\sigma} 1s^2 . \sigma 2s^2 . \overset{\bullet}{\sigma} 2s^2 . \sigma 2p_z{}^2 .$<br>$\pi 2p_x{}^2 \approx \pi 2p_y{}^2 . \overset{\bullet}{\pi} 2p_x{}^1 \approx \overset{\bullet}{\pi} 2p_y{}^1$ | $\frac{1}{2}(10-6)=2$ | Stable and Paramagnetic |
| 9. | $Ne_2$ | 20 | $\sigma 1s^2 . \overset{\bullet}{\sigma} 1s^2 . \sigma 2s^2 . \overset{\bullet}{\sigma} 2s^2 . \sigma 2p_z{}^2 .$<br>$\pi 2p_x{}^2 \approx \pi 2p_y{}^2 . \overset{\bullet}{\pi} 2p_x{}^2 \approx \overset{\bullet}{\pi} 2p_y{}^2$<br>$\overset{\bullet}{\sigma} 2p_z{}^2$ | $\frac{1}{2}(10-10)=0$ | Does not exist |

**Important**

- *$Li_2$ molecules exist in the vapour phase.*
- *In $C_2$ the double bonds consist of both pi-bonds because of the presence of 4 electrons in two pi molecular orbitals. In almost every molecule double bond is made up of a sigma bond and a pi-bond.*

## Applications of MOT

(1) In determining the stability of molecules. If $N_b$ is the number of electrons occupying bonding orbitals and $N_a$ is the number of electrons occupying the anti-bonding orbitals, then the molecule is stable if $N_b$ is greater than $N_a$.

(2) The stability of a bond order can be determined by using bond order (B.O.). It is defined as one-half the difference between the number of electrons present in the bonding and the antibonding orbitals

Bond order = $\frac{N_b - N_a}{2}$, for stable molecule bond order must be greater than zero.

(3) If all the molecular orbitals in a molecule are doubly occupied, the substance is diamagnetic otherwise, paramagnetic.

## OBJECTIVE Type Questions

[ 1 mark ]

### Multiple Choice Questions

1. Among the given species identify the isostructural pairs.

(a) [$NF_3$ and $BF_3$] (b) [$BF_4^-$ and $NH_4^+$]

(c) [$BCl_3$ and $BrCl_3$] (d) [$NH_3$ and $NO_3^-$]

[NCERT Exemplar]

**Ans.** *(b) [$BF_4^-$ and $NH_4^+$]*

**Explanation:** For $NF_3$,

$$H = \frac{(5 + 3)}{2} = 4$$

Total bond pairs: 3

Total lone pair: (4 – 3) = 1

Hybridisation: $sp^3$

Shape: Trigonal pyramidal

For $BF_3$.

$$H = \frac{(3 + 3)}{2} = 3$$

Total bond pairs: 3

Total lone pair: (3 – 3) = 0

Hybridisation: $sp^2$

Shape: Trigonal planar

For $BF_4^-$.

$$H = \frac{(3 + 4 + 1)}{2} = 4$$

Total bond pairs: 4

Total lone pair: (4 – 4) = 0

Hybridisation: $sp^3$

Shape: Tetrahedral

For $NH_4^+$.

$$H = \frac{(5 + 4 - 1)}{2} = 4$$

Total bond pairs: 4

Total lone pair: (4 – 4) = 0

Hybridisation: $sp^3$

Shape: Tetrahedral

For $BCl_3$,

$$H = \frac{(3 + 3)}{2} = 3$$

Total bond pairs: 3

Total lone pair: (3 – 3) = 0

Hybridisation: $sp^2$

Shape: Trigonal planar

For $BrCl_3$,

$$H = \frac{(7 + 3)}{2} = 5$$

Total bond pairs: 3

Total lone pairs: (5 – 3) = 2

Hybridisation: $sp^3d$

Shape: T-Shaped

For $NH_3$,

$$H = \frac{(5 + 3)}{2} = 4$$

Total bond pairs: 3

Total lone pair: (4 – 3) = 1

Hybridisation: $sp^3$

Shape: Trigonal pyramidal

For $NO_3^-$.

$$H = \frac{(5 + 0 + 1)}{2} = 3$$

Total bond pairs: 3

Total lone pair: (3 – 3) = 0

Hybridisation: $sp^2$

Shape: Trigonal planar

**Caution**

- *During calculation of the number of electron pairs, students should never forget to count the number of lone pairs.*

**2. The bond angle (in degree) of $ClF_3$ is:**

**(a) 109.5°** **(b) 104.5°**

**(c) 120°** **(d) 87.5°**

**Ans.** *(d) 87.5°*

**Explanation:** For $ClF_3$,

$$H = \frac{(7 + 3)}{2} = 5$$

Total bond pairs: 3

Total lone pairs: (5 – 3) = 2

Hybridisation: $sp^3d$

Shape: T-Shaped

So, bond angle is less than 90° in the case of T-Shaped geometry.

**3. The number of bonding and antibonding electrons in a fluorine molecule is:**

**(a) 6, 8** **(b) 8, 6**

**(c) 10, 3** **(d) 8, 10** **[Diksha]**

**Ans.** *(b) 8, 6*

**Explanation:** By applying MOT to $F_2$ molecule.

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

Total bonding electron = 10

Total antibonding electron = 8

**4. The type of hybrid orbitals of S in $SF_6$ and I in $IF_7$ respectively are:**

**(a) $sp^3d^3, sp^3d^3$** **(b) $sp^3d^2, sp^3d^3$**

**(c) $sp^3d, sp^3d$** **(d) $sp^3d^3, sp^3d^2$**

**[Diksha]**

**Ans.** *(b) $sp^3d^2, sp^3d^3$*

**Explanation:** For $SF_6$,

$$H = \frac{(6 + 6)}{2} = 6$$

Total bond pairs: 6

Total lone pair: (6 – 6) = 0

Hybridisation: $sp^3d^2$

Shape: Octahedral

For $IF_7$.

$$H = \frac{(7+7)}{2} = 7$$

Total bond pairs: 7

Total lone pair: (7 – 7) = 0

Hybridisation: $sp^3d^3$

Shape: Pentagonal bipyramidal

**5.** **Which of the following pair is expected to have the same bond order?**

(a) $O_2$, $N_2$ (b) $O_2^{\bullet}$, $N_2^-$

(c) $O_2^-$, $N_2^{\bullet}$ (d) $O_2^-$, $N_2$

[NCERT Exemplar]

**Ans.** *(b) $O_2^{\bullet}$. $N_2^-$*

**Explanation:** $O_2^{\circ}$:

$(\sigma 1s)^2(\dot{\sigma} 1s)^2(\sigma 2s)^2(\dot{\sigma} 2s)^2(\sigma 2p_z)^2(\pi 2p_x^2 = \pi 2p_y^2)$
$\dot{\pi} 2p_x^1$

$$\text{Bond order} = \frac{1}{2}\ (10 - 5) = 2.5$$

$N_2^{\circ}$:

$(\sigma 1s)^2(\dot{\sigma} 1s)^2(\sigma 2s)^2(\dot{\sigma} 2s)^2(\pi 2p_x^2 = \pi^2 p_y)(\sigma 2p_z).$
$\dot{\pi} 2p_x^1$

$$\text{Bond order} = \frac{1}{2}\ (10 - 5) = 2.5$$

**Related Theory**

- *Bond order = $\frac{1}{2}[N_b - N_a]$*

**Caution**

- *Isoelectronic species have same bond order.*

**6.** **Which one of the following molecules is expected to exhibit diamagnetic behaviour?**

(a) $C_2$ (b) $N_2$

(c) $O_2$ (d) Both (a) and (b)

**Ans.** *(d) Both (a) and (b)*

**Explanation:** By applying MOT in given molecules. $C_2$:

$\sigma 1s^2 < (\dot{\sigma} 1s^2 < \sigma 2s^2 < (\dot{\sigma} 2s^2 < (\pi 2p^2_x = \pi 2p_y^2)$

$N_2$:

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

$O_2$:

$(\sigma 1s)^2 < (\dot{\sigma} 1s)^2 < (\sigma 2s)^2 < (\dot{\sigma} 2s)^2 < (\sigma 2p_z)^2$
$(\pi 2p_x^2 = \pi 2p_y^2)\ (\dot{\pi} 2p_x = \dot{\pi} 2p_y)$

**7.** **Bond order and magnetic nature of $CN^-$ are respectively:**

(a) 3, diamagnetic

(b) 2.5, paramagnetic

(c) 3, paramagnetic

(d) 2.5, diamagnetic

**Ans.** *(a) 3, diamagnetic*

**Explanation:** Total electrons in $CN^-$: (6 + 7 + 1) = 14

$$\sigma 1s^2 < \sigma^* 1s^2 < \sigma 2s^2 < \sigma^* 2s^2 < (\pi 2p^2_x = \pi 2p^2_y) < \sigma 2p_z^2$$

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

As it has 14 electrons with all paired and no unpaired electrons, hence it is diamagnetic.

**Related Theory**

- *We can calculate bond order of molecules without using MOT diagram by calculating total number of electrons.*

| Total no. of $e^-$ | Bond Order | |
|---|---|---|
| 10 | 1 | |
| 11 | 1.5 | |
| 12 | 2 | |
| 13 | 2.5 | |
| **14** | **3** | B.O decreases |
| 15 | 2.5 | |
| 16 | 2 | |
| 17 | 1 | |
| 18 | 1 | |

**8.** **For the given molecules**

$H_2$, $Cl_2$, CO, $Br_2$, $N_2$

I II III IV V

**Choose the correct option:**

(a) I, II and IV have the same bond order.

(b) II and V have the same bond order.

(c) I and III have the same bond order.

(d) I, III and V have the same bond order.

**Ans.** *(a) I, II and IV have the same bond order.*

**Explanation:** $H_2$, $Cl_2$ and $Br_2$ are single-bonded. So, they all have same bond order equal to 1.

CO and $N_2$ are triple-bonded. So, they have bond order equal to 3.

**9.** **The paramagnetic behaviour of $B_2$ is due to the presence of:**

(a) 2 unpaired electrons in π MO

(b) 2 unpaired electrons in $\dot{\pi}$ MO

(c) 2 unpaired electrons in σ MO

(d) 2 unpaired electrons in $\dot{\sigma}$ MO

**Ans.** *(a) 2 unpaired electrons in π MO*

**Explanation:** Applying MOT for $B_2$ molecule.

$$\sigma 1s^2 < \sigma^* 1s^2 < \sigma 2s^2 < \sigma^* 2s^2 < (\pi 2p^1_x = \pi 2p^1_y)$$

**10.** **Which of the following molecules is paramagnetic in nature?**

(a) $H_2$ (b) $Li_2$

(c) $B_2$ (d) $N_2$

**Ans.** *(c) $B_2$*

**Explanation:** $B_2$ molecule has the following configuration: $\sigma 1s^2, \overset{*}{\sigma} 1s^2, \sigma 2s^2, \overset{*}{\sigma} 2s^2, \pi 2p_x^1 = \pi 2p_y^1$, and thus is paramagnetic in nature.

## Assertion - Reason (A-R)

In the following question no. (11–14), a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choice.

(a) Both (A) and (R) are true and (R) is the correct explanation of (A).

(b) Both (A) and (R) are true but (R) is not the correct explanation of (A).

(c) (A) is true but (R) is false.

(d) (A) is false but (R) is true.

**11.** **Assertion (A):** $NO^{\bullet}$ and $CN^-$ both have the same bond order and magnetism.

**Reason (R):** $NO^{\bullet}$ and $CN^-$ are isoelectronic species.

**Ans.** *(a) Both (A) and (R) are true and (R) is the correct explanation of (A).*

**Explanation:** For $NO^{\bullet}$,

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

Bond order = 3 and diamagnetic in nature.

For $CN^-$

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

Bond order = 3 and diamagnetic in nature.

**12.** **Assertion (A):** $NH_3$ molecule is $sp^3$ hybridized.

**Reason (R):** The geometry of $NH_3$ molecule is pyramidal.

**Ans.** *(b) Both (A) and (R) are true but (R) is not the correct explanation of (A).*

**Explanation:** Total electron pair: $\dfrac{(5+3)}{2} = 4$

Total bond pairs: 3

Total lone pair: (4 – 3) = 1

Clearly, $sp^3$ hybridized molecule with 3 bond pair and 1 lone pair and shape is pyramidal.

Here, due to $sp^3$ hybridisation, shape is pyramidal, not the *vice-versa*.

**13.** **Assertion (A):** When $p_x$ orbital combine with $p_y$ orbital than a sigma bond is produced.

**Reason (R):** Atomic orbitals of similar symmetry results in positive overlap.

**Ans.** *(d) (A) is false but (R) is true.*

**Explanation:** $p_x$ cannot combine with $p_y$ to form a sigma bond.

**14.** **Assertion (A):** $SF_6$ and $PF_5$ are examples of expanded octet rule.

**Reason (R):** P in $PF_5$ and S in $SF_6$ are $sp^3d$ and $sp^3d^2$ hybridisation respectively.

**Ans.** *(b) Both (A) and (R) are true but (R) is not the correct explanation of (A).*

**Explanation:** For $SF_6$,

$$H = \frac{(6+6)}{2} = 6$$

Total bond pairs: 6

Total lone pair: (6 – 6) = 0

Hybridisation: $sp^3d^2$

For $PF_5$,

$$H = \frac{(5+5)}{2} = 5$$

Total bond pairs: 5

Total lone pair: (5 – 5) = 0

Hybridisation: $sp^3d$

## CASE BASED Questions (CBQs)

[ **4** & **5** marks ]

Read the following passages and answer the questions that follow:

**15.** *The attractive force which holds the two atoms together is called a chemical bond. A covalent bond is formed by an equal sharing of electrons. A coordinate bond is also known as the dative bond is formed when an atom donates both of its electrons in a covalent bond. An ionic bond is formed by the transfer of electrons from one atom to another. Octet rule, although very useful, is not universally applicable. According to valence bond theory, a covalent bond is formed by overlapping half-filled atomic orbitals which form new orbitals of lower energy and more stability. The number of bonds between the two atoms in a molecule is called bond order. The higher the bond order* *more will be stability and bond dissociation enthalpy but the smaller the bond length. The polarity of a covalent bond depends upon the difference in electronegativity. The covalent character of a bond depends upon polarizing power. The smaller the cations and bigger the anions more will be the polarizing power. VSEPR theory helps to predict the shapes of molecules.*

**(A) Draw the structure of $XeO_4$.**

**(B) On the basis of hybridisation, draw the shape of methane $CH_4$.**

**(C) Explain the non-linear shape of $H_2S$ and non-planar shape of $PCl_3$ using valence shell electron pair repulsion theory.** **[NCERT Exemplar]**

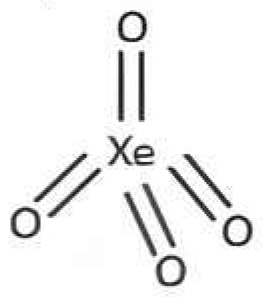
**Ans.** (A) For $XeO_4$.

$$H = \frac{(8+0)}{2} = 4$$

Total bond pairs: 4

Total lone pair: $(4 - 4) = 0$

Hybridisation of $XeO_4$ is $sp^3$ with no lone pair, so the shape is tetrahedral.



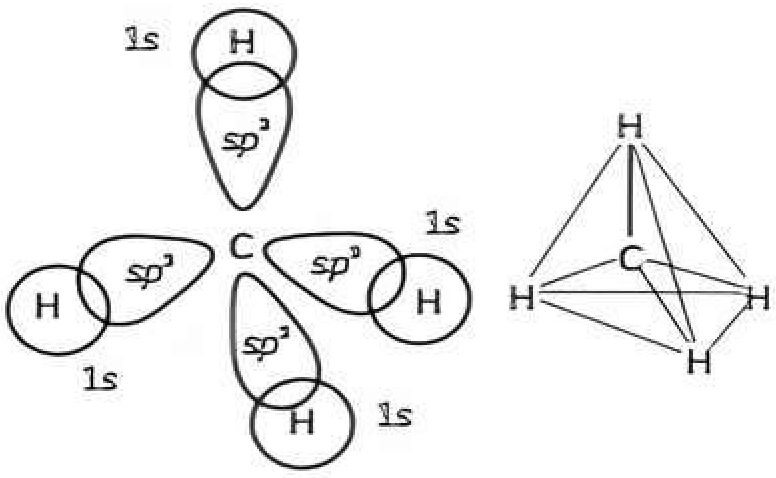
*Tetrahedral ($sp^3$)*

(B) Atomic number of C = 6

Its electronic configuration in the ground state is $1s^2 2s^2 2p_x^1 2p_y^1$

The electronic configuration of C in the excited state is $1s^2 2s^1 2p_x^1 2p_y^1 2p_z^1$

One 2s and three 2p orbitals undergo $sp^3$ hybridisation to form four $sp^3$ h-orbitals which are arranged tetrahedrally at an angle of 109.5° to each other.



*Formation and structure of methane*

(C) In $H_2S$, S is the main atom which has 2 lone pairs. These lone pairs cause repulsion and move the H-S bond away causing a non-linear shape.

The valency of P is 5 in $PCl_3$. P has 3 single bonds and 1 lone pair (pair of unshared electrons). This suggests us to use $sp^3$ hybrid orbitals on phosphorus. And the structure is non-planar due to lone pair-bond pair interactions.

**16.** *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). The energy of the antibonding orbital is raised above the parent atomic orbitals that have combined and the energy of the bonding orbital is lower than the parent atomic orbitals. Energies of various molecular orbitals for elements hydrogen to nitrogen increase in the order:*

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

*And for oxygen an elements after oxygen order of energy of molecular orbitals is given below.*

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

*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 the 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.*

**(A) Which of the following statements is correct?**

**(a) In the formation of dioxygen from oxygen atoms, ten molecular orbitals will be formed.**

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

**(c) Total number of bonding molecular orbitals will not be the same as the total number of anti-bonding orbitals in dioxygen.**

**(d) Number of filled bonding orbitals will be the same as the number of filled anti-bonding orbitals.**

**(B) Which of the following molecular orbitals has a maximum number of nodal planes?**

(a) $\sigma 1s$ (b) $\overset{*}{\sigma} 2p_z$

(c) $\sigma 2p_z$ (d) $\overset{*}{\pi} 2p_y$

**(C)** **Which of the following chemical species is most stable?**

(a) $O_2$ (b) $O_2^+$

(c) $O_2^-$ (d) $O_2^{2-}$

**[Delhi Gov. QB 2022]**

**(D)** **Which of the following order of energies of molecular orbitals is correct for $C_2$ molecule?**

(a) $(\pi 2p_x) = (\pi 2p_y) > (\sigma 2p_z) > (\pi^* 2p_x) = (\pi^* 2p_y)$

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

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

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

**(E)** **Diamagnetic species are those which contain no unpaired electrons. Which among the following is diamagnetic?**

(a) $C_2$ (b) $N_2^{2-}$

(c) $O_2$ (d) $O_2^{2-}$

**Ans.** (A) *(a) In the formation of dioxygen from oxygen atoms, ten molecular orbitals will be formed.*

**Explanation:** Applying MOT in dioxygen molecule:

$$\sigma 1s^2 \overset{*}{\sigma} 1s^2 \sigma 2s^2 \overset{*}{\sigma} 2s^2 \sigma 2p_z^2 \pi 2p_x^2 = \pi 2p_y^2 \overset{*}{\pi} 2p_x^1 = \pi 2p_y^2 \overset{*}{\sigma} 2p_z^0$$

Clearly, ten molecular orbitals are involved.

All molecular orbitals are not completely filled.

Total Number of bonding molecular orbitals will be the same as the number of anti-bonding molecular orbitals. Number of filled bonding orbitals will not be the same as the number of filled anti–bonding molecular orbitals.

(B) *(b)* $\overset{*}{\sigma} 2p_z$

**Explanation:**

$\sigma 1s$ has 1 nodal plane.

$\overset{*}{\sigma} 2p_z$ has 2 nodal planes.

$\sigma 2p_z$ has 1 nodal plane.

$\overset{*}{\pi} 2p_y$ has 1 nodal plane.

(C) *(b)* $O_2^+$

**Explanation:** $O_2^-$

$O_2^-$: $(\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p_x)^2 = (\pi 2p_y)^2(\sigma^* 2p_z)^2 (\pi^* 2p_x)^1 = (\pi^* 2p_y)^1$

$O_2^+$: $(\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p_x)^2 = (\pi 2p_y)^2(\sigma^* 2p_z)^2 (\pi^* 2p_x)^1$

$O_2^-$: $(\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p_x)^2 = (\pi 2p_y)^2(\sigma^* 2p_z)^2 (\pi^* 2p_x)^2 = (\pi^* 2p_y)^1$

$O_2^{2-}$: $(\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p_x)^2 = (\pi 2p_y)^2(\sigma^* 2p_z)^2 (\pi^* 2p_x)^2 = (\pi^* 2p_y)^2$

The most stable is $O_2^+$ due to least electrons in antibonding orbital.

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

**Explanation:** Molecules like $B_2$, $C_2$ and $N_2$. Energy of $\sigma 2p_z$ molecular orbital is greater than that of $\pi 2p_x$ and $\pi 2p_y$ molecular orbitals.

(E) *(d)* $O_2^{2-}$

**Explanation:**

The MOT diagram for $O_2^{2-}$ is $(\sigma 1s)^2(\overset{*}{\sigma} 1s)^2(\sigma 2s)^2(\overset{*}{\sigma} 2s)^2(\sigma 2p_z)^2(\pi 2p_x^2 = \pi 2p_y^2)(\overset{*}{\pi} 2p_x^2 = \overset{*}{\pi} 2p_y^2)$

as there are no unpaired electron thus, it has diamagnetic character.

## VERY SHORT ANSWER Type Questions (VSA)

[ 1 mark ]

**17.** **What is the magnetic character of anion of $KO_2$? [Delhi Gov. QB 2022]**

**Ans.** This is paramagnetic in nature.

$O_2^-$: $(\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p_x)^2 = (\pi 2p_y)^2(\sigma^* 2p_z)^2 (\pi^* 2p_x)^2 = (\pi^* 2p_y)^1$.

**18.** **Why $H_2$ molecule exists but not $He_2$ molecules? [Diksha]**

**Ans.** Bond order of $H_2$ molecule = 1

Bond order of $He_2$ molecule = 0

Hence, the $H_2$ molecule exists but not $He_2$ molecule.

**19.** **Define bond order.**

**Ans.** Bond order (B.O.) is defined as one-half the difference between the number of electrons present in the bonding and the antibonding orbitals.

**20.** **Define bonding molecular orbital.**

**Ans.** In MOT, bonding orbitals are formed by constructive interference of atomic orbitals and they have lower energy than atomic orbitals.

**21.** **Why $NH_3$ and $BF_3$ have different shapes?**

**Ans.** $NH_3$ has three bond pairs and one lone pair but $BF_3$ has 3 bond pairs only but no lone pair. Hence they have different shapes.

## SHORT ANSWER Type-I Questions (SA-I)

[ **2** marks ]

**22. Give a reason why $H_2^+$ ions are more stable than $H_2^-$ though they have the same bond order.**

**Ans.** Bond order of $H_2^+$: $\frac{(1-0)}{2} = 0.5$

Bond order of $H_2^-$: $\frac{(2-1)}{2} = 0.5$

$H_2^-$ has one electron in its anti-bonding orbital. As a result, $H_2^-$ is less stable than $H_2^+$ though they have the same bond order.

**23. How would the bond lengths vary in the following species?**

**$C_2$, $C_2^{2-}$, $C_2^+$**

**Ans.** Bond order of $C_2$ : 3

Bond order of $C_2^{2-}$ : 2

Bond order of $C_2^+$ : 2.5

Bond length is inversely proportional to bond order. So, order of bond length is $C_2 < C_2^+ < C_2^{2-}$

**24. What are zero overlaps?**

**Ans.** The conditions for overlapping are the minimum energy difference between orbitals and their proper orientation. When these two conditions are not full-filled, orbitals cannot overlap each other. This is called zero overlapping. For example, $P_x$ and $P_y$ orbitals of $O_2$ molecules cannot overlap with each other due to different orientations.

**25. Explain on the basis of molecular orbital theory, why $Be_2$ does not exist.**

**Ans.** Electronic configuration of $Be_2$ molecule $\sigma 1s^2$, $\overset{*}{\sigma} 1s^2$, $\sigma 2s^2$, $\overset{*}{\sigma} 2s^2$.

$$\text{Bond order} = \frac{1}{2}(N_b - N_a) = \frac{1}{2}(4 - 4) = 0$$

Since bond order is zero, so $Be_2$ does not exist.

**26. Why are bonding molecular orbitals more stable than anti-bonding molecular orbitals?**

**Ans.** Bonding orbitals are formed by constructive interference of atomic orbitals so they have lower energy than the corresponding atomic orbitals but anti-bonding orbitals are formed by destructive interference of atomic orbitals so they have higher energy than the corresponding orbitals. That's why bonding orbitals are more stable than anti-bonding orbitals.

## SHORT ANSWER Type-II Questions (SA-II)

[ **3** marks ]

**27. What do you understand about hybridisation? Give examples.**

**Ans.** The intermixing of pure atomic orbitals to produce new hybrid orbitals of equal energies for bonding purposes is called hybridisation. The concept of hybridisation can't apply to isolated atoms. It is used to explain the bonding in a molecule. It is a hypothetical concept in which the number of hybrid orbitals generated is equal to the number of pure atomic orbitals that participate in the hybridisation process. For example, $BeF_2$ has *sp* hybridisation in which one s and one *p*-orbital undergo hybridisation to form two *sp* hybrid orbitals.

**28. Write the hybridisation of each carbon atom of the following molecule.**

$$\overset{1}{H_3C} - \overset{2}{CH} = \overset{3}{C} = \overset{4}{CH_2}$$

**Ans.** For $C_1$, total sigma bonds are four, so, hybridisation is $sp^3$.

For $C_2$, total sigma bonds are three, so, hybridisation is $sp^2$.

For $C_3$, total sigma bonds are two, so, hybridisation is *sp*.

For $C_4$, total sigma bonds are three, so, hybridisation is $sp^2$.

**29. $CO_2$ is linear whereas $SO_2$ is bent-shaped. Give a reason.**

**Ans.** For $CO_2$,

$$H = \frac{(4+0)}{2} = 2$$

Total bond pairs: 2

Total lone pair: (2 – 2) = 0

Hybridisation: *sp*

Shape: linear

For $SO_2$,

$$H = \frac{(6+0)}{2} = 3$$

Total bond pair: 2

Total lone pair: (3 – 2) = 1

Hybridisation: $sp^2$

Shape: bent-shape

**30. Using molecular orbital theory, compare the bond energy and magnetic character of $O_2^+$ and $O_2^-$ species. [NCERT Exemplar]**

**Ans.** For $O_2^+$.

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

Bond order = $\frac{(10-5)}{2}$ = 2.5. and paramagnetic in nature

For $O_2^-$.

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

Bond order: $\frac{(10-7)}{2}$ = 1.5. and paramagnetic in nature.

Since, bond order is directly proportional to bond energy, bond energy of $O_2^+$ is greater than that of $O_2^-$.

## LONG ANSWER Type Questions (LA)

[ **4** & **5** marks ]

**31. Write the difference between valence bond and molecular bond theories.**

**Ans.**

| S.No. | Valence Bond Theory | Molecular Orbital Theory |
|---|---|---|
| (1) | Bonding is explained with help of atomic orbitals. | Bonding is explained with the help of molecular orbitals. |
| (2) | Only half-filled orbitals of the valence shell take part in bonding. | All the electrons in given atoms take part in bonding. |
| (3) | The concept of resonance is applicable. | Resonance has no role in MOT. |
| (4) | It fails to explain the paramagnetic character of $O_2$. | It explains the paramagnetic character of $O_2$. |
| (5) | Calculation is simple. | It is difficult to apply. |

**32. Give electronic configuration and calculate their bond order and predict their paramagnetic behaviour.**

**(A)** $H_2^+$ **(B)** $Li_2$

**(C)** $B_2$ **(D)** $C_2$

**(E)** $C_2$

**Ans.** (A) $H_2^+(1) = (\sigma\ 1s)^1$

Bond order = $\frac{1}{2}(1-0) = \frac{1}{2}$, paramagnetic

(B) $Li_2(6) = \sigma 1s^2 \overset{*}{\sigma} 1s^2 \sigma 2s^2$

Bond order = $\frac{1}{2}(4-2) = 1$, diamagnetic

(C) $B_2(10) = \sigma 1s^2 \overset{*}{\sigma} 1s^2 \sigma 2s^2 \overset{*}{\sigma} 2s^2 \pi 2p_x^{\ 1} = \pi 2p_y^{\ 1}$

Bond order = $\frac{1}{2}(6-4) = 1$, paramagnetic

(D) $C_2(12) = \sigma 1s^2 \overset{*}{\sigma} 1s^2 \sigma 2s^2 \overset{*}{\sigma} 2s^2 \pi 2p_x^{\ 2} = \pi 2p_y^{\ 2}$

Bond order = $\frac{1}{2}(8-4) = 2$, diamagnetic

(E) $N_2(14) = \sigma 1s^2 \overset{*}{\sigma} 1s^2 \sigma 2s^2 \overset{*}{\sigma} 2s^2 \pi 2p_x^{\ 2} = \pi 2p_y^{\ 2}\ \sigma 2p_z^{\ 2}$

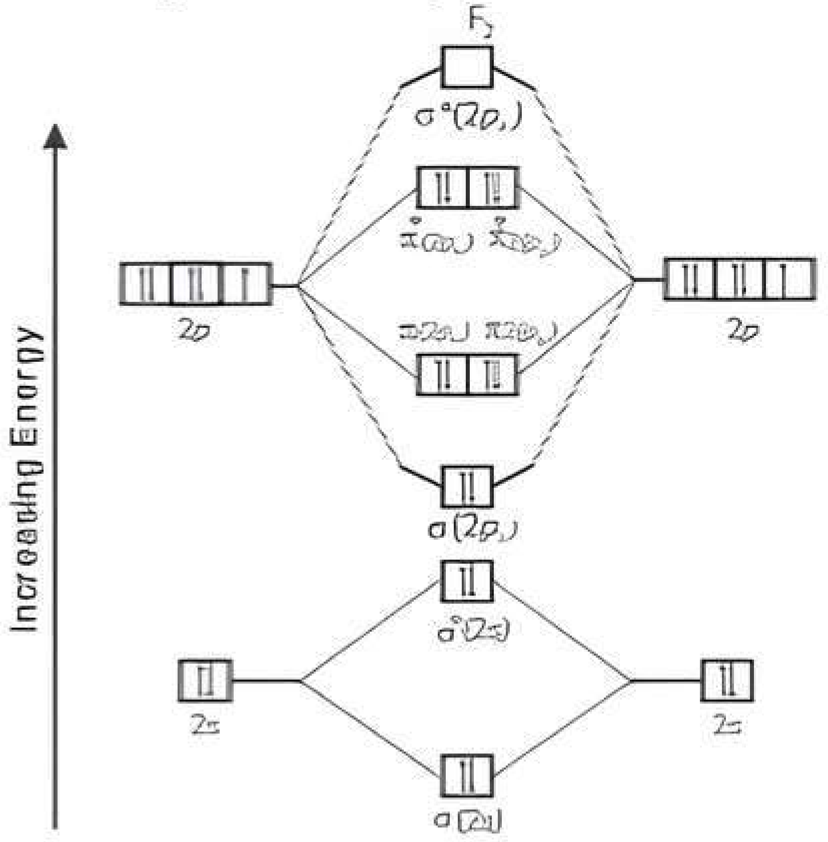
Bond order = $\frac{1}{2}(10-4) = 3$, diamagnetic

**33. Using molecular orbital energy level diagram to show $F_2$ have a single bond, $Ne_2$ no bond and $N_2$, a triple bond. [NCERT Exemplar]**

**Ans.** Formation of $F_2$ molecule

$_9F = 1s^2, 2s^2, 2p_x^{\ 2}, 2p_y^{\ 2}, 2p_z^{\ 1}$

$F_2$ molecule $\sigma 1s^2, \overset{*}{\sigma} 1s^2, \sigma 2s^2, \overset{*}{\sigma} 2s^2, \sigma 2p_z^{\ 2}, \pi 2p_x^{\ 2} = \pi 2p_y^{\ 2}, \overset{*}{\pi} 2p_x^{\ 2} = \overset{*}{\pi} 2p_y^{\ 2}$



*Molecular orbital diagram of $F_2$ molecule*

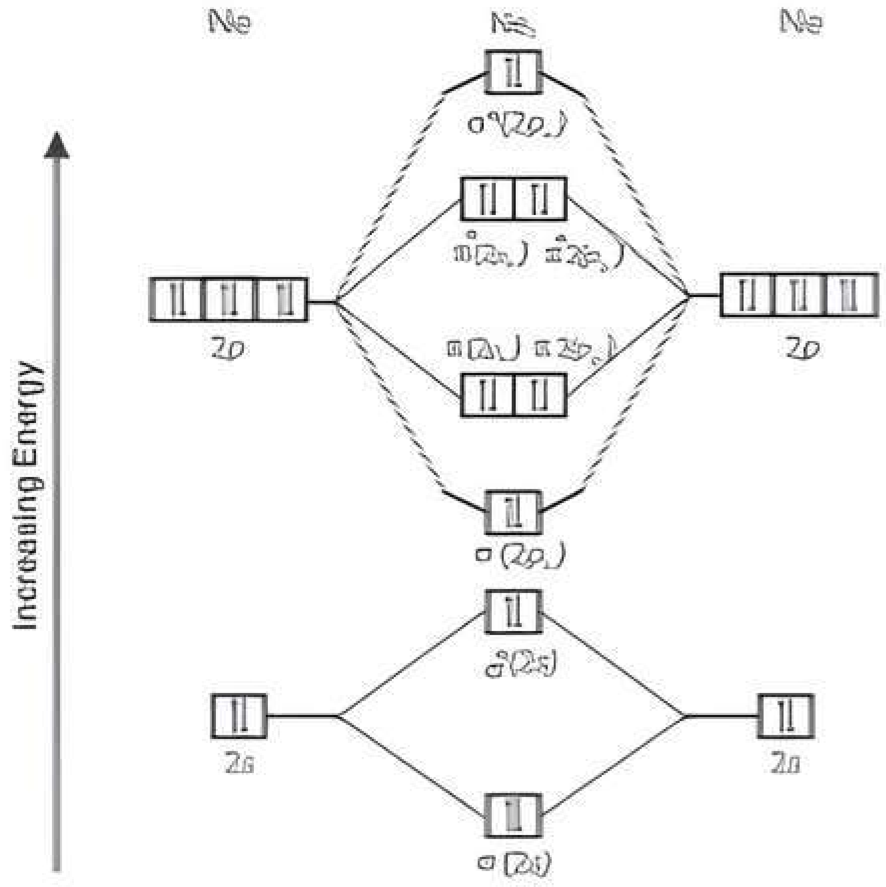
Bond order = $\frac{1}{2}(N_b - N_a) = \frac{1}{2}(10-8) = 1$

Bond order value 1 means that $F_2$ contains single bond.

Formation of $Ne_2$ molecule

$_{10}Ne = 1s^2 . 2s^2 . 2px^2 . 2py^2 . 2pz^2$

$Ne_2 = \sigma 1s^2 , \overset{*}{\sigma} 1s^2 . \sigma 2s^2 . \overset{*}{\sigma} 2s^2 . \sigma 2p_z{}^2 . \pi 2p_x{}^2 = \pi 2p_y{}^2 \overset{*}{\pi} 2p_x{}^2 = \overset{*}{\pi} 2p_y{}^2 \overset{*}{\sigma} 2p_z{}^2$



*Molecular orbital diagram of $Ne_2$ molecule*

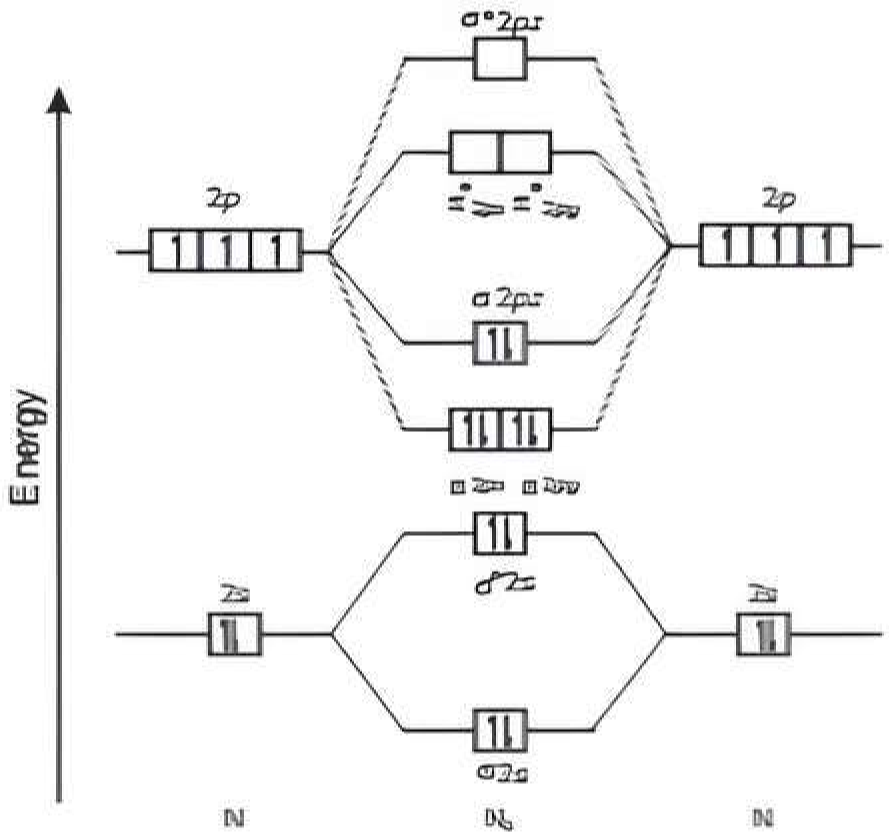
Bond order $= \frac{1}{2}\ (N_b - N_a) = \frac{1}{2}\ (10 - 10) = 0$

Bond order value zero means that there is no formation of bond between two Ne atoms. Hence. $Ne_2$ the molecule does not exist.

Formation of $N_2$ molecule :

$_7N = 1s^2 . 2s^2 . 2p_x{}^1 . 2p_y{}^1 . 2p_z{}^1$

$N_2 = \sigma 1s^2 . \overset{*}{\sigma} 1s^2 . \sigma 2s^2 . \overset{*}{\sigma} 2s^2 \pi 2p_x{}^2 = \pi 2p_y{}^2 \sigma 2p_z{}^2$



*Molecular orbital diagram of $N_2$ molecule*

Bond order $= \frac{1}{2}\ (N_b - N_a) = \frac{1}{2}\ (10 - 4) = 3$

Bond order 3 means that $N_2$ contains a triple bond.

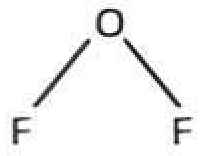
**34. Draw the structure of $OF_2$ with the help of VSEPR theory. State the type of hybridisation of the central atom and geometry of molecule. Write the oxidation states of O and F. [Diksha]**

**Ans.** Total electron pairs $\frac{(6+2)}{2} = 4$

Total bond pairs: 2

Total lone pair: $(4 - 2) = 2$

Hybridisation: $sp^3$ and shape is bent shape



Oxidation state of F: −1

Since overall molecule is neutral, $x + 2(-1) = 0$

$x = +2$ which is equal to the oxidation state of O.

**35. What is the sum of the bond pairs and lone pairs around Br in $BrO_4^-$ ion?**

**Ans.** Total electron pairs $\frac{(7+1+0)}{2} = 4$

Total bond pairs: 4

Total lone pairs: $(4 - 4) = 0$

Thus, sum of bond pair and lone pair: 4.

**36. Out of $B_2$, $C_2$, $N_2$, $N_2^+$, $O_2^-$; how many species are paramagnetic?**

**Ans.** $B_2$: $\sigma 1s^2 < \overset{*}{\sigma} 1s^2 < \sigma 2s^2 < \overset{*}{\sigma} 2s^2 < \pi 2p^1 = \pi 2p^1)$

$C_2$: $\sigma 1s^2 < \overset{*}{\sigma} 1s^2 < \sigma 2s^2 < \overset{*}{\sigma} 2s^2 < \pi 2p_x^2 = \pi 2p_y^2$

$N_2$: $\sigma 1s^2 < \overset{*}{\sigma} 1s^2 < \sigma 2s^2 < \overset{*}{\sigma} 2s^2 < \pi 2p_x^2 = \pi 2p_y^2$
$< \sigma 2p_z$

$N_2^+$: $\sigma 1s^2 < \overset{*}{\sigma} 1s^2 < \sigma 2s^2 < \overset{*}{\sigma} 2s^2 < \pi 2p_x^2 = \pi 2p_y^2$
$< \sigma 2p_z^1$

$O_2^-$: $\sigma 1s^2 < \overset{*}{\sigma} 1s^2 < \sigma 2s^2 < \overset{*}{\sigma} 2s^2 < \sigma 2p_z^2 < \pi 2p_x^2$
$= \pi 2p_y^2 < \overset{*}{\pi} 2p_x^2 = \overset{*}{\pi} 2p_y^1$

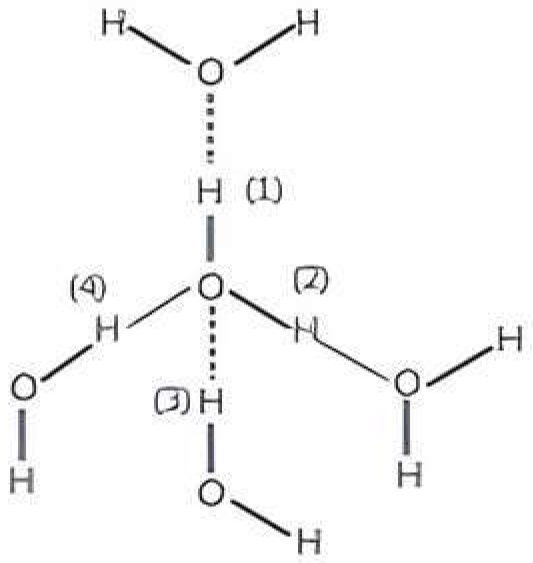
Clearly, 3 of them are paramagnetic.

# HYDROGEN BONDING

# 5

## Hydrogen Bonding

Have you ever thought about how water molecules are bonded together and what kind of bonding they have? In $H_2O$ molecule, the central oxygen atom is covalently linked to two H-atoms through a bond called hydrogen bond. The attractive force which binds hydrogen atom of one molecule with the electronegative atom (F, O, or N) of another molecule, is called hydrogen bonding. Each H-atom can form a hydrogen bond. In addition to these two hydrogen bonds, the central oxygen atom also forms two hydrogen bonds with the neighbouring molecules. Therefore, four hydrogen bonds are formed by a single molecule of water as shown below.



These bonds are represented by a dotted line. E.g., in case of HF molecule, the hydrogen bond exists between hydrogen atom of one molecule and fluorine atom of another molecule as shown below:

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

Here, hydrogen bond behaves like a bridge between two atoms that holds one atom by a covalent bond and the other by a hydrogen bond.

### Cause of Formation of Hydrogen Bond

When a hydrogen atom is bonded to a highly electronegative atom through a covalent bond, the electronegative atom tries to pull the shared pair electrons towards its own side resulting in the development of a large partial negative charge on the electronegative atom and a corresponding partial positive charge on the hydrogen atom. Now, the positively charged hydrogen atom of one molecule may attract the negatively charged atom of some other molecule and the two molecules can be linked together through a weak force of attraction. This weak force of attraction is known as the hydrogen bonding.

Hydrogen bond is much weaker as compared to a covalent bond. The magnitude of H-bonding also depends on the physical state of the compound. In case of solids, it is maximum and for gases, it is minimum. Thus, the hydrogen bonds have a great influence on the structure and the physical properties of the compounds.

### Conditions for Hydrogen Bonding

A hydrogen bond is formed when the following conditions are satisfied.

(1) **High electronegative atom is bonded to hydrogen:** The molecule must have an atom of high electronegativity such as F, O or N directly bonded to hydrogen atom as present in HF, $H_2O$ and $NH_3$.

(2) **Small size of the electronegative atom:** The size of the electronegative atom should be quite small because a smaller atom attracts the bonded electron pair strongly.

**Example 5.1:** Case Based:

*The weak attractive force which binds the partially positively charged hydrogen atom of one molecule, with the partially negatively charged atom of some other molecule of a similar or different type, or with some other negative centre of the same molecule; is referred to as hydrogen bond or hydrogen bonding. For effective hydrogen bonding, it is necessary that the size of the electronegative atom is small. If the size of the electronegative atom is large, its attraction on the bonded pair will be less. Consequently, less polarity will be developed in the molecule and the resulting hydrogen bond will be weaker. And also, hydrogen atoms should be bonded to a highly electronegative atom such as F, O, or N. The higher the electronegativity of the atom bonded to hydrogen, the greater is the strength of hydrogen bond. Since the electronegativities of F, O, or N follow the order F > O > N, the strength of hydrogen bond decreases in the order.*

$$H ---- F > H —— O > H —— N$$

**(A) Though covalent in nature, methanol is soluble in water, why?**

**(a) Methanol is transparent like water.**

**(b) Due to hydrogen bonding between methanol and water molecules.**

**(c) Due to van der Waal's forces between methanol and water.**

**(d) Due to covalent attractive forces.**

(B) Which of the following compounds show maximum hydrogen bonding?

(a) HF (b) $H_2O$

(c) $NH_3$ (d) $CH_3OH$

(C) Explain why hydrogen bonding does not exist in HCl although Cl is quite electronegative.

(D) What factors lead to the formation of hydrogen bonding with elements N and O.

(E) **Assertion (A):** Hydrogen bond is much weaker as compared to a covalent bond.

**Reason (R):** The bond energy of a covalent bond is usually of the order of 400 kJ $mol^{-1}$.

(a) Both (A) and (R) are true and (R) is the correct explanation of (A).

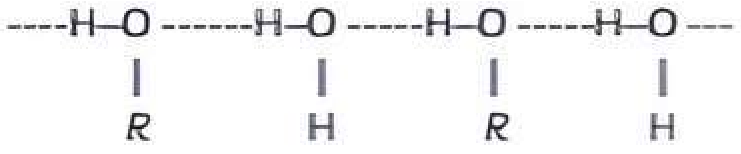
(b) Both (A) and (R) are true but (R) is not the correct explanation of (A).

(c) (A) is true but (R) is false.

(d) (A) is false but (R) is true.

**Ans.** (A) *(b) Due to hydrogen bonding between methanol and water molecules.*

**Explanation:** Methanol is soluble in water due to the presence of hydrogen bonding between methanol and water.



$$\begin{array}{llll} \text{----H–O ------} & \text{H–O -----} & \text{H–O -----} & \text{H–O ---} \\ \quad\ | & \quad | & \quad | & \quad | \\ \quad\ R & \quad H & \quad R & \quad H \end{array}$$

In methanol, *R* is – $CH_3$ group.

(B) *(a) HF*

**Explanation:** Greater the electronegativity and the smaller the size of the atom, the stronger is the H–bond.

(C) HCl does not form hydrogen bonding in spite of being highly electronegative because of the large difference in the electronegativity of H and Cl atoms.

## ⚠ Caution

- *Many times, students think that HCl is soluble in water, as it forms H-bonding. But the fact is that since it is ionic compound completely dissociates into its ions and thus, is soluble in water.*

(D) Because of the high electronegativity of the elements N and O resulting in the development of a large partial negative charge on the electronegative atom and a corresponding partial positive charge on the hydrogen atoms lead to formation of hydrogen bonds.

(E) *(b) Both (A) and (R) are true but (R) is not the correct explanation of (A).*

**Explanation:** The bond energy of a hydrogen bond lies between 3.5 – 40 kJ $mol^{-1}$.

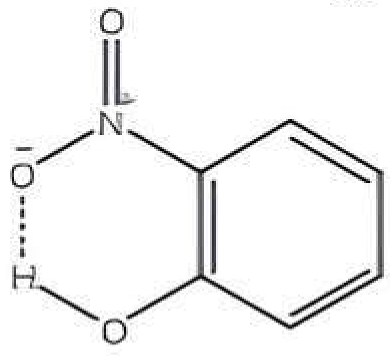
## Types of H–Bonds

There are two types of H–bonds:

(1) **Intermolecular Hydrogen Bond:** Hydrogen bond that exists between two molecules of the same or different substances known as Intermolecular hydrogen bond. Some examples of the compounds containing such type of bond are: Hydrogen fluoride molecule, Alcohol, Water, Ice.

This type of bonding results in increased melting points, boiling points and solubility.

(2) **Intramolecular Hydrogen Bond:** Such a bond exists within the same molecule. In this type of hydrogen bonding, a hydrogen bond is formed between a hydrogen atom covalently attached to some electronegative atom and some other electronegative atom (F, O, N) present close to it in the same molecule. It results in the cyclisation of the molecule. *e.g.*, o–nitrophenol



*o-nitrophenol*

This bonding prevents the association of molecules, making the molecule contract. Hence, it decreases melting point, boiling point and solubility. *e.g.*, o–nitrophenol has a lower boiling point than p–nitrophenol.

**Example 5.2:** **Define hydrogen bond. Is it weaker or stronger than the van der Waals forces? [NCERT]**

**Ans.** The attractive force which binds hydrogen atom of one molecule with the electronegative atom (F, O, or N) of another molecule, is called hydrogen bond.

Hydrogen bond is stronger than the van der Waals forces.

**Example 5.3:** **Case Based:**

*The hydrogen bonding that occurs in water leads to some unusual, but very important properties. Most molecular compounds that have a mass similar to water are gases at room temperature. Because of the strong hydrogen bonds, water molecules are able to stay condensed in the liquid state. In the liquid state, the hydrogen bonds of water can break and reform as the molecules flow from one place to another. When water is cooled, the molecules begin to slow down. Eventually, when water is frozen to ice, the hydrogen bonds become permanent and form a very specific network. The bent shape of the molecules* *leads to gaps in the hydrogen bonding network of ice. Ice has the very unusual property that its solid state is less dense than its liquid state. Ice floats on liquid water. Virtually all other substances are denser in the solid-state than in the liquid state. Hydrogen bonds play a very important biological role in the physical structures of proteins and nucleic acids.*

(A) The ice floats on water because:

- (a) Solids have lesser density than liquids.
- (b) It has an open cage-like structure in which lesser molecules are paced per mL than water.
- (c) Ice is lighter than water.
- (d) When ice is formed water molecules come closer and start floating.

(B) What is the maximum number of hydrogen bonds in which a water molecule can participate?

- (a) 1
- (b) 2
- (c) 3
- (d) 4

(C) Explain why water has maximum density at 4°C?

(D) How does the shape of $H_2O$ affect its properties?

(E) Assertion (A): When ethyl alcohol ($C_2H_5OH$) is dissolved in water, the molecules of the two substances get associated through intermolecular hydrogen bonding.

Reason (R): Intermolecular hydrogen bonding is also possible between the molecules of different substances.

- (a) Both (A) and (R) are true and (R) is the correct explanation of (A).
- (b) Both (A) and (R) are true but (R) is not the correct explanation of (A).
- (c) (A) is true but (R) is false.
- (d) (A) is false but (R) is true.

**Ans.** (A) *(b) It has an open cage-like structure in which lesser molecules are placed per mL than water.*

**Explanation:** Density of ice is less than water due to an open cage structure formed by hydrogen bonding.

**Related Theory**

➥ *The X-ray diffraction studies of ice suggest that in it, each $H_2O$ molecule is surrounded by the oxygen atoms of four neighbouring $H_2O$ molecules.*

(B) *(d) 4*

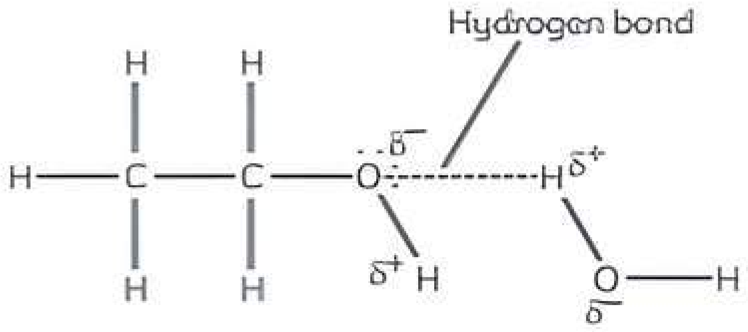
**Explanation:** In $H_2O$ molecule, the central oxygen atom is covalently linked to two H-atoms. Each H-atom can form a hydrogen bond. In addition to these two hydrogen bonds, the central oxygen atom also forms two hydrogen bonds with the neighbouring molecules. Therefore, four hydrogen bonds are formed by a single molecule of water.

(C) This is because on heating ice, the hydrogen bonds break up progressively and the molecules start packing more closely in the vacant spaces. Above this temperature, the normal expansion of the liquid more than compensates Thus, increasing in density.

(D) The bond angle in $H_2O$ is 104.5° which makes it in bent shape. $H_2O$ forms angle with H-atom at tips and O atom at corner. Because of the high electronegativity of O atoms develop a partial negative charge. And due to this bent shape, the $H_2O$ is polar.

(E) *(a) Both (A) and (R) are true and (R) is the correct explanation of (A).*

**Explanation:** During intermolecular hydrogen bonding, bonds exist between two molecules of the same or different substances.



## OBJECTIVE Type Questions

[ 1 mark ]

### Multiple Choice Questions

1. Which of the following statements is true about hydrogen bonding?
   - (a) Cl and H have a difference in electronegativities yet there is no H-bonding in HCl because size of Cl is large.
   - (b) Intermolecular H-bonding results in a decrease in m.p and b.p.
   - (c) Ice has maximum density at 0°C due to H-bonding.
   - (d) $KHCl_2(HCl_2^-)$ exists but $KHF_2(HF_2^-)$ does not exist due to a lack of H-bonding in HCl.

**Ans.** *(a) Cl and H have a difference in electronegativities yet there is no H-bonding in HCl because size of Cl is large.*

**Explanation:** For hydrogen bonding, the size of the atom should be small.

2. **In which of the following molecules will the hydrogen bond be strongest?**

(a) $H_2S$ (b) HI
(c) $H_2O$ (d) HCl

[NCERT Exemplar]

**Ans.** *(c) $H_2O$*

**Explanation:** Only $H_2O$ forms H-bonding while other substances HCl, HI and $H_2S$ do not form H-bonding.

3. **Which of the following has the strongest bond?**

(a) HF (b) HCl
(c) HBr (d) HI

**Ans.** *(a) HF*

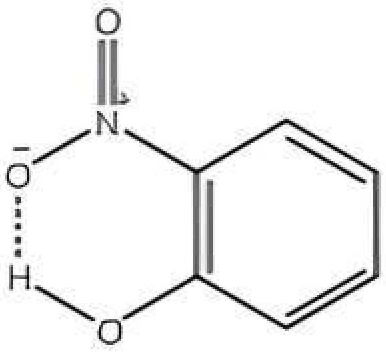
**Explanation:** Due to the largest difference in electronegativity, H—F bond is strongest.

4. **Which of the following molecules show intramolecular hydrogen bonding?**

(a) *o*–nitrophenol (b) *p*–nitrophenol
(c) Benzoic acid (d) Ethanol

**Ans.** *(a) o–nitrophenol*

**Explanation:** Intramolecular hydrogen bonding exists within the molecule. Among the given options only *o*-nitrophenol shows intramolecular H-bonding.



*o–nitrophenol*

### Related Theory

- *o-Nitrophenol is steam volatile due to intramolecular hydrogen bonding. Thus, it has lower melting than p-nitrophenol.*

5. **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:**

(a) $HF > H_2O > NH_3$ (b) $H_2O > HF > NH_3$
(c) $NH_3 > HF > H_2O$ (d) $NH_3 > H_2O > HF$

[NCERT Exemplar]

**Ans.** *(a) $HF > H_2O > NH_3$*

**Explanation:** Hydrogen bond is formed due to the difference in electronegativities. As the electronegativity difference increases, strength of hydrogen bonding increases. The higher the hydrogen bonding, the higher is the boiling point. Thus, order of boiling point is $HF > H_2O > NH_3$.

6. **Which of the following observations can be explained on the basis of hydrogen bonding?**

(I) HF has a higher boiling point than other halogen acids.
(II) $H_2O$ has highest boiling point among hydrides of group 16 elements.
(III) $NH_3$ has a lower boiling point than $PH_3$.

**Select the correct option:**

(a) (I), (II) and (III) (b) (I) and (III)
(c) (II) and (III) (d) (I) and (II)

**Ans** *(d) (I) and (II)*

**Explanation:** Statement (III) is not true since $NH_3$ has a higher boiling point than $PH_3$ due to hydrogen bonding.

7. **Hydrogen fluoride dissociates in water to give .......... .**

(a) Hydrogen and fluorine atom
(b) Difluoride ion
(c) Fluoride ion
(d) None of the above [Diksha]

**Ans.** *(b) Difluoride ion*

**Explanation:** Hydrogen fluoride dissociates in waterm due to intermolecular H-bonding.

8. **Which of the following substances have abnormally high boiling points and why?**

(a) $H_2S$ (b) HF
(c) HI (d) $CH_4$

**Ans.** *(b) HF*

**Explanation:** HF due to intermolecular hydrogen bonding has abnormally high boiling point.

## Assertion - Reason (A-R)

In the following question no. (9–11), a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choice.

(a) Both (A) and (R) are true and (R) is the correct explanation of (A).
(b) Both (A) and (R) are true but (R) is not the correct explanation of (A).
(c) (A) is true but (R) is false.
(d) (A) is false but (R) is true.

**9. Assertion (A):** Boiling point of *p*–nitrophenol is greater than that of *o*–nitrophenol.

**Reason (R):** There is intermolecular hydrogen bonding in *p*-nitrophenol and intermolecular hydrogen bonding in *o*–nitrophenol.

**Ans.** *(c) (A) is true but (R) is false.*

**Explanation:** There is intermolecular hydrogen bonding in *p*-nitrophenol and intramolecular hydrogen bonding in *o*-nitrophenol. As intramolecular hydrogen bonding in *o*-nitrophenol prevents further association, it has a lower boiling point than *p*–nitrophenol.

**10. Assertion (A):** $NH_3$ has the highest boiling point in the hydride of group 15.

**Reason (R):** $NH_3$ shows strong intermolecular hydrogen bonding.

**Ans.** *(d) (A) is false but (R) is true.*

**Explanation:** Down the group, the boiling point of hydrides generally increases due to increase in van der Waals forces. But due to the presence of H-bonding in $NH_3$, its boiling point is higher than that of $PH_3$ as well as $AsH_3$ but von der Waals forces in bigger Sb molecules dominate the H-bonding in $NH_3$ and therefore, the boiling point of $SbH_3$ is greater than that of $NH_3$.

The correct order of boiling point of group 15 hydrides is $PH_3 < AsH_3 < NH_3 < SbH_3 < BiH_3$.

**11. Assertion (A):** Alcohols in spite of being covalent compounds are soluble in water.

**Reason (R):** Compounds whose molecules are able to form hydrogen bonding with water are soluble in them.

**Ans.** *(a) Both (A) and (R) are true and (R) is the correct explanation of (A).*

**Explanation:** Because their molecules can form intermolecular hydrogen bonding with water molecules.

## CASE BASED Questions (CBQs)

[ **4** & **5** marks ]

Read the following passages and answer the questions that follow:

**12.** *When we consider the boiling points of molecules, we usually expect molecules with larger molar masses to have higher normal boiling points than molecules with smaller molar masses. This, without taking hydrogen bonds into account, is due to greater dispersion forces. Larger molecules have more space for electron distribution and thus more possibilities for an instantaneous dipole moment.*

(A) Identify the hydride which has the lowest boiling point.

(a) $NH_3$ (b) $PH_3$

(c) $SbH_3$ (d) $AsH_3$

(B) The hydrogen bonding is strongest in:

(a) O–H -----S (b) S–H ——O

(c) F–H ——F (d) F–H ——O

(C) What is the reason behind the higher boiling point of water?

(a) Covalent bonding

(b) Co-ordinate bonding

(c) Hydrogen bonding

(d) Electrostatic force of attraction

(D) The boiling increases with increase in ........ of a substance.

(a) intramolecular hydrogen bonding

(b) molecular mass

(c) intermolecular hydrogen bonding

(d) both (b) and (c)

(E) H-bonding couldn't affect the boiling point of:

(a) HI (b) $NH_3$

(c) $H_2O$ (d) $CH_3OH$

**Ans.** (A) *(b) $PH_3$*

**Explanation:** As the hydrogen bonding is absent in $PH_3$ molecule in a liquid state, it has the lowest boiling point.

(B) *(c) F–H ------F*

**Explanation:** The hydrogen bonding is strongest in F–H ------F because of high electronegativity of fluorine.

(C) *(c) Hydrogen bonding*

**Explanation:** In $H_2O$ molecule, the central oxygen atom is covalently linked to two H-atoms. Each H-atom can form a hydrogen bond. In addition to these two hydrogen bonds, the central oxygen atom also forms two hydrogen bonds with the neighbouring molecules. Therefore the reason behind the higher boiling point of water is hydrogen bonding.

(D) *(d) both (b) and (c)*

**Explanation:** Due to intermolecular hydrogen bonding molecules associate which increases the boiling point of substance.

(E) *(a) HI*

**Explanation:** Hydrogen bonding exists only when a compound has electronegative atoms like N, O, F atoms. Atoms which are larger in size don't show hydrogen bonding because they don't have high electron density.

**13.** *Highly electronegative atoms like N, O, F cannot completely remove the valence electron from hydrogen and form an ion because there are no core electrons in hydrogen. Removing the hydrogen's 1s electron would produce a subatomic particle, the proton, whose small size results in a high charge density that would pull back the electron. So it will not happen. The result is that hydrogen forms polar covalent bonds when attached to an electronegative atom and does not form ions. The electronegative atoms pull on the valence electron "Deshields" the hydrogen's proton resulting in a large δ+ charge over a small area. A highly electronegative atom has a large δ– charge and if it has a lone pair of electrons, they are strongly attracted to the "deshielded proton" of another hydrogen and create a hydrogen bond. It should also be noted that the small size of the hydrogen allows it to move in real close, resulting is a strong bonding interaction.*

**(A) Answer the following questions:**

**(i) Will all H atoms form H-bonds?**

**(ii) Why is H-bond strength more in peroxide than water?**

**(B) How chloroform makes hydrogen bond with acetone?**

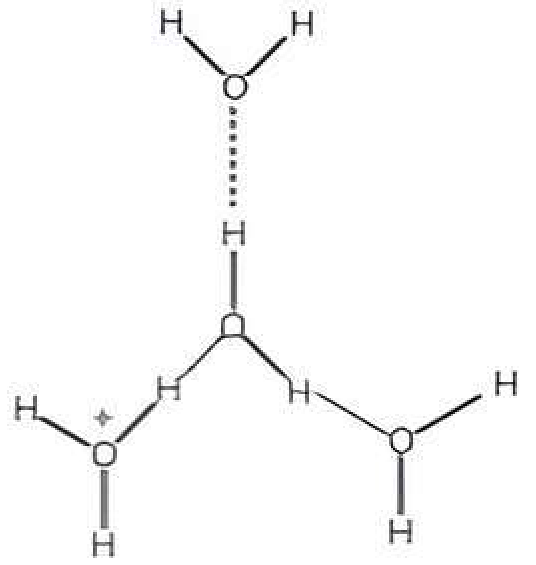
**(C) How many numbers of hydrogen bonds are present in $H_3O^+$? Draw structure also.**

**Ans.** (A) (i) A molecule that has a hydrogen atom attached to some electronegative atom will form hydrogen bonding.

(ii) Due to one additional oxygen atom in peroxide, the strength of the hydrogen bond is more than water.

(B) Due to the presence of three chlorine atoms in chloroform, the carbon atom becomes partially positive, so it pulls away the electron density from the hydrogen atom to balance electron distribution, thereby making the hydrogen atom partially positive. Hence, the oxygen atom of acetone which is partially negative interacts to form hydrogen bonding.

(C) 3 hydrogen bonds are present in $H_3O^+$.



## VERY SHORT ANSWER Type Questions (VSA)

[ 1 mark ]

**14. Why $KHF_2$ exists but $KHCl_2$ does not?**

**Ans.** Due to H-bonding in H—F, we have

H—F ----H—F ----H—F ----

This can dissociate to give $HF_2^-$ ion and hence $KHF_2$ exists but there is no H-bonding in H—Cl. So $HCl_2^-$ ion does not exist and hence, $KHCl_2$ also does not exist.

**15. Among the covalent bond and hydrogen bond, which bond has a higher bond length?**

**Ans.** The bond length of a hydrogen bond is greater than that of a covalent bond.

**16. At room temperature $H_2O$ exist as liquid while $H_2S$ exist as a gas. Give reason.**

**Ans.** $H_2O$ is liquid because of its association due to the hydrogen bonding which is not possible in $H_2S$ due to bigger size of sulphur.

**17. Does the presence of intramolecular hydrogen bonding affects the boiling point of a liquid?**

**Ans.** No, because it does not associate with the molecules.

## SHORT ANSWER Type-I Questions (SA-I)

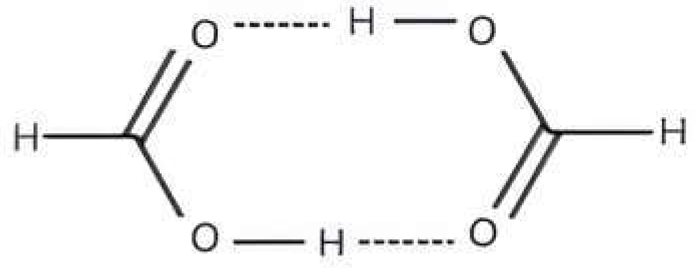
[ 2 marks ]

**18. Explain why HF is less viscous than $H_2O$.**

**Ans.** There is greater intermolecular hydrogen bonding in $H_2O$ than that in HF as each $H_2O$ molecule forms four H-bonds with other water molecules whereas HF forms only two H-bonds with other HF molecules. The greater the intermolecular H-bonding, the greater is the viscosity. Hence, HF is less viscous than $H_2O$.

**19. Why does formic acid exist as a dimer? What is its one consequence?**

**Ans.** Formic acid exists as a dimer because of hydrogen bonding.



*Formic acid dimer*

## SHORT ANSWER Type-II Questions (SA-II)

[ 3 marks ]

**20. Explain why glycerol ($CH_2OH.CHOH.CH_2OH$) is more viscous than ethyl alcohol ($C_2H_5OH$).**

**Ans.** Glycerol ($CH_2OH.CHOH.CH_2OH$) possesses three–OH groups while ethyl alcohol possesses only one–OH group. Hence, hydrogen bonding is more extensive in glycerol as compared to that in ethyl alcohol. This is why glycerol is more viscous than ethyl alcohol.

**21. Arrange the following bonds in order of increasing ionic character by giving a reason.**

**N—H, F—H, C—H and O—H**

**Ans.** The greater the difference in electronegativity between two atoms bonded together, greater the ionic character.

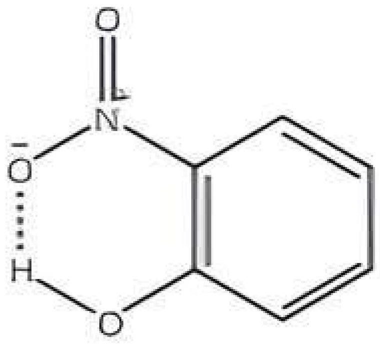
Therefore, increasing order of ionic character of the given bonds is as follows:

HF (1.9) >OH (1.4) > NH (0.9) > CH (0.4)

Therefore, increasing order of ionic character of the given bonds is as follows:

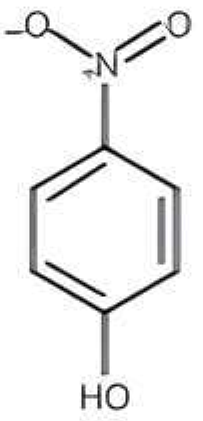
C–H < N–H < O–H < F–H.

**22. Here is the structure of molecules of two different compounds.**



*o–nitrophenol*

(I)



(II)

**(A) Which of the two compounds will show intramolecular H-bonding and which will show intermolecular H-bonding?**

**(B) Which of the given compounds will have a higher melting point?**

**(C) Which will form H-bond with water easily and is soluble in it?**

**[NCERT Exemplar]**

**Ans.** (A) Compound (I) will show intramolecular H-bond. Intramolecular H-bonding is shown when a hydrogen atom exists within a molecule. In compound (I), the hydrogen atom is in between the two oxygen atoms. And compound (II), *p*–nitrophenol will show intermolecular H-bond. In compound (II), a hydrogen bond is found between a hydrogen atom of one molecule attached to some electronegative atom and O atom of another molecule.

(B) Intermolecular bonding allows the association of molecules, making the molecule expand. Hence, in compound (II), *p*-nitrophenol will have a higher melting point.

(C) Molecules of *p*-nitrophenol (compound II) will form intermolecular H-bonding with water easily, so it results in increased solubility with water. While *o*–nitrophenol (compound I) due to intramolecular H-bonding with itself is not able to associate with water easily, thus its solubility is less in water.

## LONG ANSWER Type Questions (LA)

[ **4** & **5** marks ]

**23. What is a hydrogen bond? What requirements should a molecule fulfil for the formation of a hydrogen bond? Discuss intramolecular and intermolecular hydrogen bonds.**

**Ans.** When a hydrogen atom is bonded to a highly electronegative atom through a covalent bond, the electronegative atom tries to pull the shared pair of electrons towards its own side resulting in the development of a large partial negative charge on the electronegative atom and a corresponding partial positive charge on the hydrogen atom. Now, the positively charged hydrogen atom of one molecule may attract the negatively charged atom of some other molecule and the two molecules can be linked together through a weak force of attraction. This weak force of attraction is known as hydrogen bonding.

A hydrogen bond is much weaker as compared to a covalent bond. The magnitude of H-bonding also depends on the physical state of the compound. In the case of solids, it is maximum and for gases, it is minimum. Thus, the hydrogen bonds have a great influence on the structure and the physical properties of the compounds.

**Conditions for Hydrogen Bonding**

A hydrogen bond is formed when the following conditions are satisfied.

(1) High electronegativity of atom bonded to hydrogen: The molecule must have an atom of high electronegativity such as F, O or N directly bonded to hydrogen atom as present in HF, $H_2O$ and $NH_3$

(2) Small size of the electronegative atom: The size of the electronegative atom should be quite small because a smaller atom attracts the bonded electron pair strongly.

**Types of H-Bonds:**

There are two types of H-bonds

**(1) Intermolecular Hydrogen Bond:** Hydrogen bond that exists between two molecules of the same or different substances. Some examples of the compounds containing such types of bonds are:

- Hydrogen fluoride
- Alcohol
- Water
- Ice

It results in increased melting, boiling points and solubility.

**(2) Intramolecular Hydrogen Bond:** Such a bond exists within the same molecule. In the case of this type of hydrogen bonding, a hydrogen bond is formed between a hydrogen atom covalently attached to some electronegative atom and some other electronegative atom (F, O, N) present close to it in the same molecule. It results in the cyclisation of the molecule. *e.g.*, *o*–nitrophenol.