4

Chemical Bonding and Molecular Structure

Facts that Matter

• Chemical Bond

The force that holds different atoms in a molecule is called chemical bond.

• Octet Rule

Atoms of different elements take part in chemical combination in order to complete their octet or to attain the noble gas configuration.

• Valence Electrons

It is the outermost shell electron which takes part in chemical combination.

• Facts Stated by Kössel in Relation to Chemical Bonding

- In the periodic table, the highly electronegative halogens and the highly electropositive alkali metals are separated by noble gases.
- Formation of an anion and cation by the halogens and alkali metals are formed by gain of electron and loss of electron respectively.
- Both the negative and positive ions acquire the noble gas configuration.
- The negative and positive ions are stabilized by electrostatic attraction

  Example,

$$\begin{array}{rcl}
\underset{[\mathrm{Ne}]\,3s^1}{\mathrm{Na}} & \longrightarrow & \underset{[\mathrm{Ne}]}{\mathrm{Na}^+} + e^- \\
\underset{[\mathrm{Ne}]\,3s^2\,3p^5}{\mathrm{Cl}} + e^- & \longrightarrow & \underset{[\mathrm{Ne}]\,3s^2\,3p^6 \quad \text{or} \quad [\mathrm{Ar}]}{\mathrm{Cl}^-} \\
\mathrm{Na}^+ + \mathrm{Cl}^- & \longrightarrow & \mathrm{NaCl}.
\end{array}$$

• Modes of Chemical Combination

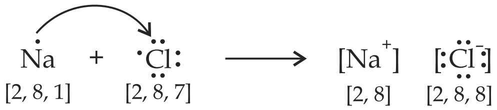
- **By the transfer of electrons:** The chemical bond which formed by the complete transfer of one or more electrons from one atom to another is termed as electrovalent bond or ionic bond.
- **By sharing of electrons:** The bond which is formed by the equal sharing of electrons between one or two atoms is called covalent bond. In these bonds electrons are contributed by both.
- **Co-ordinate bond:** When the electrons are contributed by one atom and shared by both, the bond is formed and it is known as dative bond or co-ordinate bond.

• Ionic or Electrovalent Bond

Ionic or Electrovalent bond is formed by the complete transfer of electrons from one atom to another. Generally, it is formed between metals and non-metals. We can say that it is the electrostatic force of attraction which holds the oppositely charged ions together.

The compounds which is formed by ionic or electrovalent bond is known as electrovalent compounds. *For Example,*

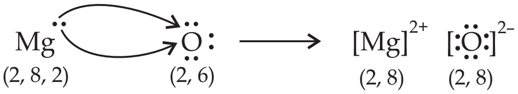
(*i*) NaCl is an electrovalent compound. Formation of NaCl is given below:



or NaCl

Na^+ ion has the configuration of Ne while Cl^- ion represents the configuration of Ar.

(*ii*) Formation of magnesium oxide from magnesium and oxygen.



Electrovalency: Electrovalency is the number of electrons lost or gained during the formation of an ionic bond or electrovalent bond.

• Factors Affecting the Formation of Ionic Bond

(*i*) **Ionization enthalpy:** As we know that ionization enthalpy of any element is the amount of energy required to remove an electron from outermost shell of an isolated gaseous atom to convert it into cation.

Hence, lesser the ionization enthalpy, easier will be the formation of a cation and have greater chance to form an ionic bond. Due to this reason alkali metals have more tendency to form an ionic bond.

For example, in formation of Na^+ ion I.E = 496 kJ/mole

While in case of magnesium, it is 743 kJ/mole. That's why the formation of positive ion for sodium is easier than that of magnesium.

Therefore, we can conclude that lower the ionization enthalpy, greater the chances of ionic bond formation.

(*ii*) **Electron gain enthalpy** (Electron affinities): It is defined as the energy released when an isolated gaseous atom takes up an electron to form anion. Greater the negative electron gain enthalpy, easier will be the formation of anion. Consequently, the probability of formation of ionic bond increases.

For example. Halogens possess high electron affinity. So, the formation of anion is very common in halogens.

$$\begin{aligned} Cl\,(g) + e^- &\longrightarrow Cl^- \;\; 348 \text{ kJ/mole.} \\ &= -348 \text{ kJ mol}^{-1}. \\ \Delta_{eg}H &= -ve \end{aligned}$$

(*iii*) **Lattice energy or enthalpy:** It is defined as the amount of energy required to separate 1 mole of ionic compound into separate oppositely charged ions.

Lattice energy of an ionic compound depends upon following factors:

(*i*) **Size of the ions:** Smaller the size, greater will be the lattice energy.

(*ii*) **Charge on the ions:** Greater the magnitude of charge, greater the interionic attraction and hence higher the lattice energy.

• General Characteristics of Ionic Compounds

(*i*) **Physical State:** They generally exist as crystalline solids, known as crystal lattice. Ionic compounds do not exist as single molecules like other gaseous molecules e.g., H_2, N_2, O_2, Cl_2 etc.

(*ii*) **Melting and boiling points:** Since ionic compounds contain high interionic force between them, they generally have high melting and boiling points.

(*iii*) **Solubility:** They are soluble in polar solvents such as water but do not dissolve in organic solvents like benzene, CCl_4 etc.

(*iv*) **Electrical conductivity:** In solid state they are poor conductors of electricity but in molten state or when dissolved in water, they conduct electricity.

(*v*) **Ionic reactions:** Ionic compounds produce ions in the solution which gives very fast reaction with oppositely charged ions.

For example,

$$Na^+Cl^-(aq) + Ag^+NO_3^-(aq) \longrightarrow AgCl\downarrow(s) + NaNO_3(aq)$$

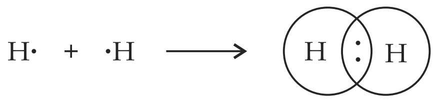
• Covalent Bond—Lewis-Langmuir Concept

When the bond is formed between two or more atoms by mutual contribution and sharing of electrons, it is known as covalent bond.

If the combining atoms are same the covalent molecule is known as homoatomic. If they are different, they are known as heteroatomic molecule.

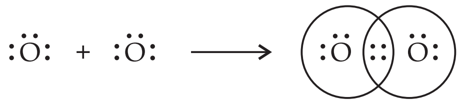
For Example,

(*i*) Formation of hydrogen molecule.



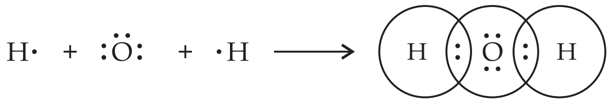
or $H-H$

(*ii*) Formation of oxygen molecule.



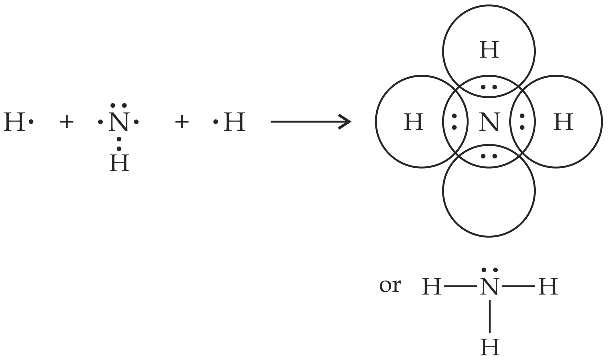
or $:\ddot{O}=\ddot{O}:$

(*iii*) Formation of H_2O molecule.



or $H-O-H$

(*iv*) Formation of NH_3 molecule.



• Lewis Representation of Simple Molecules (the Lewis Structures)

The Lewis dot Structure can be written through the following steps:

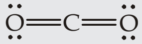
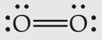
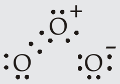
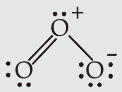
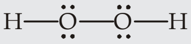
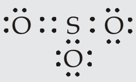
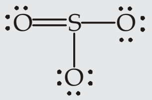
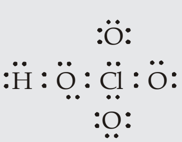
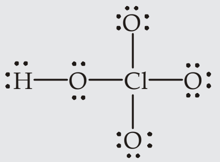
(*i*) Calculate the total number of valence electrons of the combining atoms.

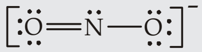
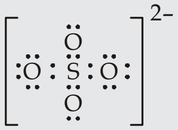
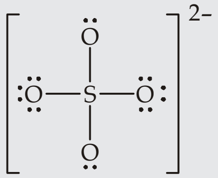
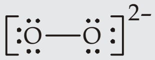
(*ii*) Each anion means addition of one electron and each cation means removal of one electron. This gives the total number of electrons to be distributed.

(*iii*) By knowing the chemical symbols of the combining atoms.

(*iv*) After placing shared pairs of electrons for single bond, the remaining electrons may account for either multiple bonds or as lone pairs. It is to be noted that octet of each atom should be completed.

Lewis structures of some typical molecules and ions

Molecule/Ion		*Lewis Representation*		
(*i*)	CO		or	
(*ii*)	CO_2		or	
(*iii*)	O_2		or	
(*iv*)	O_3		or	
(*v*)	H_2O_2		or	
(*vi*)	SO_3		or	
(*vii*)	$HClO_4$ (Perchloric acid)		or	

(*viii*)	CN^- (Cyanide ion)		or	
(*ix*)	NO_2^- (Nitrite ion)		or	
(*x*)	SO_4^{2-}		or	
(*xi*)	O_2^{2-}		or	

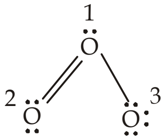
- **Formal Charge**

In polyatomic ions, the net charge is the charge on the ion as a whole and not by particular atom. However, charges can be assigned to individual atoms or ions. These are called formal charges.

It can be expressed as

$$\begin{array}{l}\text{Formal charge (F.C.)}\\\text{on an atom in a Lewis}\\\text{structure}\end{array} = \left[\begin{array}{l}\text{total number of valence}\\\text{electrons in the free}\\\text{atom}\end{array}\right] - \left[\begin{array}{l}\text{total number of non}\\\text{bonding (lone pair)}\\\text{electrons}\end{array}\right] - (1/2)\left[\begin{array}{l}\text{total number of}\\\text{bonding (shared)}\\\text{electrons}\end{array}\right]$$

It does not indicate the real charge. Let us consider the Ozone molecule (O_3). The Lewis structure of O_3 may be drawn as:



The atoms have been numbered as 1, 2 and 3. The formal charge on:

The central O atom marked 1

$$= 6 - 2 - \frac{1}{2}(6) = +1$$

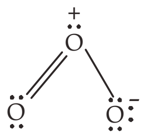
The end O atom marked 2

$$= 6 - 4 - \frac{1}{2}(4) = 0$$

The end O atom marked 3

$$= 6 - 6 - \frac{1}{2}(2) = -1$$

Hence, we represent O_3 along with the formal charges as follows:



• Limitations of the Octet Rule

(*i*) **The incomplete octet of the central atoms:** In some covalent compounds central atom has less than eight electrons. *i.e.,* it has an incomplete octet. *For example,*

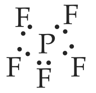
$$\mathrm{Li:Cl} \quad \mathrm{H:Be:H} \quad \mathrm{Cl:\overset{\overset{Cl}{..}}{B}:Cl}$$

Li, Be and B have 1, 2, and 3 valence electrons only.

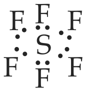
(*ii*) **Odd-electron molecules:** There are certain molecules which have odd number of electrons the octet rule is not applied for all the atoms.

$$\ddot{\mathrm{N}}=\ddot{\mathrm{O}} \qquad \ddot{\mathrm{O}}=\overset{+}{\mathrm{N}}-\ddot{\mathrm{O}}^{-}$$

(*iii*) **The expanded Octet:** In many compounds there are more than eight valence electrons around the central atom. It is termed as expanded octet. *For Example,*



PF_5 (10 electrons)



PF_6 (12 electrons)

• Other Drawbacks of Octet Theory

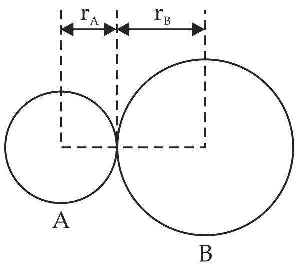
(*i*) Some noble gases, also combine with oxygen and fluorine to form a number of compounds like XeF_2, $XeOF_2$ etc.

(*ii*) This theory does not account for the shape of the molecule.

(*iii*) It does not give any idea about the energy of the molecule and relative stability.

• Bond Length

It is defined as the equilibrium distance between the centres of the nuclei of the two bonded atoms. It is expressed in terms of Å. Experimentally, it can be defined by X-ray diffraction or electron diffraction method.



The bond length in a covalent molecule AB.
$R = r_A + r_B$ (R is the bond length and r_A and r_B are the covalent radii of atoms A and B respectively)

• Bond Angle

It is defined as the angle between the lines representing the orbitals containing the bonding electrons.

It helps us in determining the shape. It can be expressed in degree. Bond angle can be experimentally determined by spectroscopic methods.

• 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.

Bond Enthalpy is also known as bond dissociation enthalpy or simple bond enthalpy. Unit of bond enthalpy = kJ $mol^{-1.}$

Greater the bond enthalpy, stronger is the bond. For *e.g.,* the H—H bond enthalpy in hydrogen is 435.8 kJ mol^{-1}.

The magnitude of bond enthalpy is also related to bond multiplicity. Greater the bond multiplicity, more will be the bond enthalpy. For *e.g.,* bond enthalpy of C—C bond is 347 kJ mol^{-1} while that of C = C bond is 610 kJ mol^{-1}.

In polyatomic molecules, the term mean or average bond enthalpy is used.

Average Bond Enthalpies of some common Bonds

Bond	*Bond enthalpy (kJ mol^{-1})*	*Bond*	*Bond enthalpy (kJ mol^{-1})*
H—H	435.8	C–C	347
Cl—Cl	239	C = C	610
Br—Br	196	C ≡ C	836
I—I	158	N—N	158
H—Cl	431.0	N = N	418
H—F	564	N ≡ N	946

• 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. *For example,*

Bond order of H_2 (H—H) = 1

Bond order of O_2 (O = O) = 2

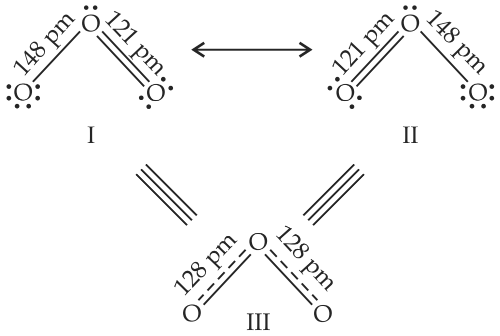
Bond order of N_2 (N ≡ N) = 3

Isoelectronic molecules and ions have identical bond orders. For example, F_2 and O_2^{2-} have bond order = 1· N_2, CO and NO^+ have bond order = 3. With the increase in bond order, bond enthalpy increases and bond length decreases. *For example,*

For N_2 B.O. = 3
Bond enthalpy = 946 kJ/mol.
For O_2, B.O. = 2
Bond enthalpy = 498 kJ/mol.

• Resonance Structures

There are many molecules whose behaviour cannot be explained by a single-lewis structure, For example, Lewis structure of Ozone represented as follows:

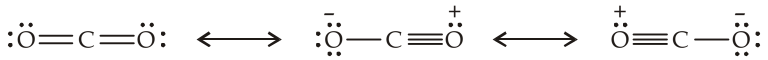


Resonance in the O_3 molecule
(Structures I and II represent the two canonical forms while the Structure III is the resonance hybrid)

Thus, according to the concept of resonance, whenever a single Lewis structure cannot explain all the properties of the molecule, the molecule is then supposed to have many structures with similar energy. Positions of nuclei, bonding and nonbonding pairs of electrons are taken as the canonical structure of the hybrid which describes the molecule accurately. For O_3, the two structures shown above are canonical structures and the III structure represents the structure of O_3 more accurately. This is also called resonance hybrid.

Some resonating structures of some more molecules and ions are shown as follows:

Carbon dioxide (CO_2)

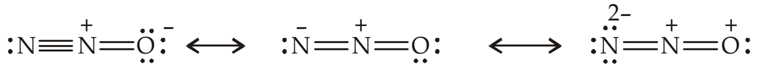


$$O=C=O \longleftrightarrow \overset{-}{O}-C\equiv\overset{+}{O} \longleftrightarrow \overset{+}{O}\equiv C-\overset{-}{O}$$

Carbon monoxide (CO)

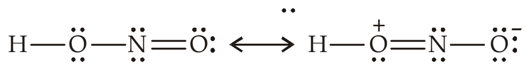
$$C=O \longleftrightarrow \overset{+}{C}-\overset{-}{O} \longleftrightarrow \overset{-}{C}\equiv\overset{+}{O}$$

Nitrous oxide (N_2O)



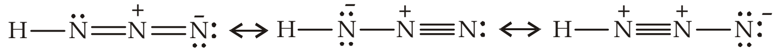
$$N\equiv\overset{+}{N}=\overset{-}{O} \longleftrightarrow \overset{-}{N}=\overset{+}{N}=O \longleftrightarrow \overset{2-}{N}=\overset{+}{N}=\overset{+}{O}$$

Nitrous acid (HONO)



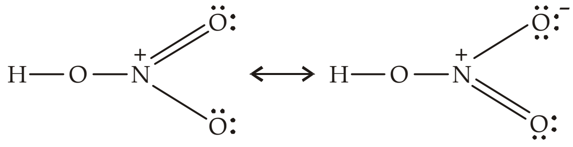
$$H-O-N=O \longleftrightarrow H-\overset{+}{O}=N-\overset{-}{O}$$

Hydrazoic acid (HN_3)



$$H-N=\overset{+}{N}=\overset{-}{N} \longleftrightarrow H-\overset{-}{N}-\overset{+}{N}\equiv N \longleftrightarrow H-\overset{+}{N}\equiv\overset{+}{N}-\overset{-}{N}$$

Nitric acid (HNO_3)



• Polarity of Bonds

Polar and Non-Polar Covalent bonds

Non-Polar Covalent bonds: When the atoms joined by covalent bond are the same like; H_2, O_2, Cl_2, the shared pair of electrons is equally attracted by two atoms and thus the shared electron pair is equidistant to both of them.

Alternatively, we can say that it lies exactly in the centre of the bonding atoms. As a result, no poles are developed and the bond is called as non-polar covalent bond. The corresponding molecules are known as non-polar molecules.

For Example,

$$\begin{array}{cc} H:H & :\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}: \\ (H-H) & (Cl-Cl) \end{array}$$

Polar bond: When covalent bonds formed between different atoms of different electronegativity, shared electron pair between two atoms gets displaced towards highly electronegative atoms.

For Example, in HCl molecule, since electronegativity of chlorine is high as compared to hydrogen thus, electron pair is displaced more towards chlorine atom, thus chlorine will acquire a partial negative charge (δ^-) and hydrogen atom have a partial positive charge (δ^+) with the magnitude of charge same as on chlorination. Such covalent bond is called polar covalent bond.

$$\overset{\delta^+}{H}-\overset{\delta^-}{Cl}$$

Greater the difference in electronegativity of the bonding atoms, more will be the polarity of the bond.

$$\overset{\delta+}{H}-\overset{\delta-}{F} \quad > \quad \overset{\delta+}{H}-\overset{\delta-}{Cl} \quad > \quad \overset{\delta+}{H}-\overset{\delta-}{Br}$$

- **Dipole Moment**

Due to polarity, polar molecules are also known as dipole molecules and they possess dipole moment. Dipole moment is defined as the product of magnitude of the positive or negative charge and the distance between the charges.

$$\text{Dipole Moment } (\mu) = \text{Charge } (Q) \times (d) \text{ (Distance of Separation)}$$

It is expressed in Debye units (D)

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

Dipole moment is a vector quantity. It is depicted by a small arrow with tail on positive centre and head pointing towards the negative centre. *For Example,*

$$\overset{\longrightarrow}{H-F}$$

With the help of dipole moment the degree of polarity of bonds can be expressed.

- **Applications of Dipole Moment**

(*i*) For determining the polarity of the molecules.

(*ii*) In finding the shapes of the molecules.

For example, the molecules with zero dipole moment will be linear or symmetrical. Those molecules which have unsymmetrical shapes will be either bent or angular. (*e.g.,* NH_3 with $\mu = 1.47$ D).

(*iii*) In calculating the percentage ionic character of polar bonds.

• The Valence Shell Electron Pair Repulsion (VSEPR) Theory

Sidgwick and Powell in 1940, proposed a simple theory based on repulsive character of electron pairs in the valence shell of the atoms. It was further developed by Nyholm and Gillespie (1957).

Main Postulates are the following:

(*i*) The exact shape of molecule depends upon the number of electron pairs (bonded or non bonded) around the central atoms.

(*ii*) The electron pairs have a tendency to repel each other since they exist around the central atom and the electron clouds are negatively charged.

(*iii*) Electron pairs try to take such position which can minimize the rupulsion between them.

(*iv*) The valence shell is taken as a sphere with the electron pairs placed at maximum distance.

(*v*) A multiple bond is treated as if it is a single electron pair and the electron pairs which constitute the bond as single pairs.

• Valence Bond Theory

Valence bond theory was introduced by Heitler and London (1927) and developed by Pauling and others. It is based on the concept of atomic orbitals and the electronic configuration of the atoms.

Let us consider the formation of hydrogen molecule based on valence-bond theory.

Let two hydrogen atoms A and B having their nuclei N_A and N_B and electrons present in them are e_A and e_B.

As these two atoms come closer new attractive and repulsive forces begin to operate.

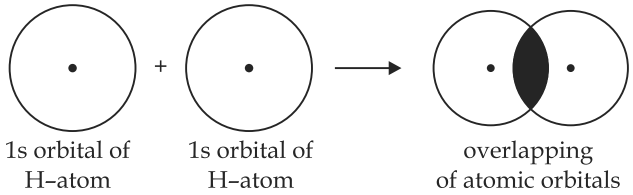
(*i*) The nucleus of one atom is attracted towards its own electron and the electron of the other and vice versa.

(*ii*) Repulsive forces arise between the electrons of two atoms and nuclei of two atoms.

Attractive forces tend to bring the two atoms closer whereas repulsive forces tend to push them apart.

• Orbital Overlap Concept

According to orbital overlap concept, covalent bond formed between atoms results in the overlap of orbitals belonging to the atoms having opposite spins of electrons. Formation of hydrogen molecule as a result of overlap of the two atomic orbitals of hydrogen atoms is shown in the figures that follows:



Stability of a Molecular orbital depends upon the extent of the overlap of the atomic orbitals.

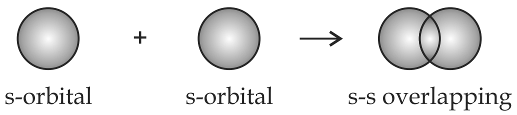
• Types of Orbital Overlap

Depending upon the type of overlapping, the covalent bonds are of two types, known as sigma (σ) and pi (π) bonds.

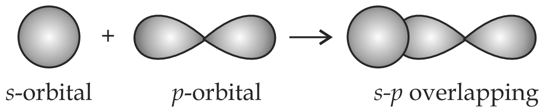
(*i*) **Sigma (σ bond):** Sigma bond is formed by the end to end (head-on) overlap of bonding orbitals along the internuclear axis.

The axial overlap involving these orbitals is of three types:

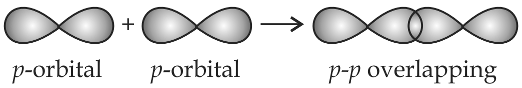
- ***s-s* overlapping:** In this case, there is overlap of two half-filled *s*-orbitals along the internuclear axis as shown below:



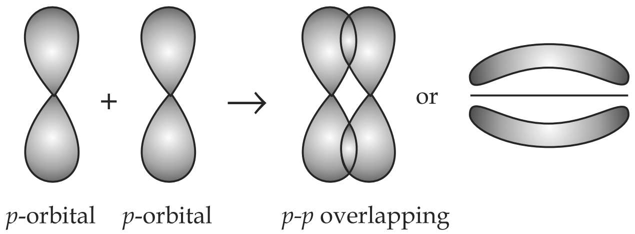
- ***s-p* overlapping:** This type of overlapping occurs between half-filled *s*-orbitals of one atom and half filled *p*-orbitals of another atoms.



- ***p-p* overlapping:** This type of overlapping takes place between half filled *p*-orbitals of the two approaching atoms.



(*ii*) **pi (π bond):** π bond is formed by the atomic orbitals when they overlap in such a way that their axes remain parallel to each other and perpendicular to the internuclear axis.The orbital formed is due to lateral overlapping or sidewise overlapping.



• Strength of Sigma and *pi* Bonds

Sigma bond (σ bond) is formed by the axial overlapping of the atomic orbitals while the π-bond is formed by sidewise overlapping. Since axial overlapping is greater as compared to sidewise. Thus, the sigma bond is said to be stronger bond in comparison to a π-bond.

Distinction between sigma and π bonds

Sigma (σ) Bond	*pi (π) Bond*
(1) s–orbitals are involved in the formation of σ bond.	(1) s-orbitals are not involved in the bond formation.
(2) The overlap is quite large and the bond formed is strong.	(2) π bond is comparatively weak.
(3) The bond is formed by axial overlap of atomic orbitals.	(3) The bond is formed by the sidewise overlap of atomic orbitals.
(4) Only one lobe of the p-orbitals is involved	(4) Both lobes of *p*-orbitals are involved in the overlap.
(5) The electron cloud formed in symmetry.	(5) The electron cloud is unsymmetrical.

- **Hybridisation**

Hybridisation is the process of intermixing of the orbitals of slightly different energies so as to redistribute their energies resulting in the formation of new set of orbitals of equivalent energies and shape.

Salient Features of Hybridisation:

(*i*) Orbitals with almost equal energy take part in the hybridisation.

(*ii*) Number of hybrid orbitals produced is equal to the number of atomic orbitals mixed.

(*iii*) Geometry of a covalent molecule can be indicated by the type of hybridisation.

(*iv*) The hybrid orbitals are more effective in forming stable bonds than the pure atomic orbitals.

Conditions necessary for hybridisation:

(*i*) Orbitals of valence shell take part in the hybridisation.

(*ii*) Orbitals involved in hybridisation should have almost equal energy.

(*iii*) Promotion of electron is not necessary condition prior to hybridisation.

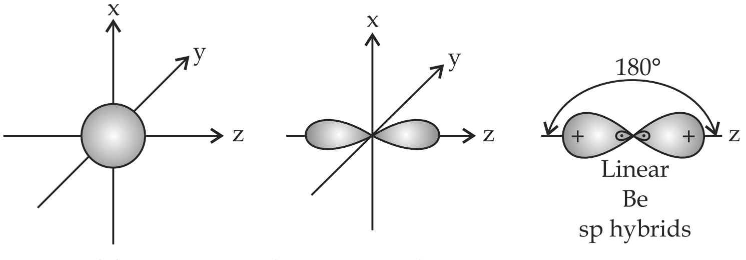
(*iv*) In some cases filled orbitals of valence shell also take part in hybridisation.

Types of Hybridisation:

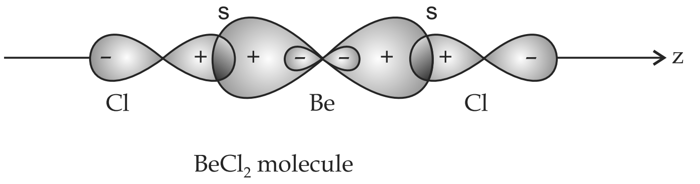
(*i*) **sp hybridisation:** When one *s* and one p-orbital hybridise to form two equivalent orbitals, the orbital is known as *sp* hybrid orbital, and the type of hybridisation is called *sp* hybridisation.

Each of the hybrid orbitals formed has 50% s–characer and 50%, p–character. This type of hybridisation is also known as diagonal hybridisation.

Examples: All compounds of carbon containing $C \equiv C$ triple bond like acetylene (C_2H_2), $BeCl_2$, BeF_2, BeH_2 etc.



(a) Formation of sp hybrids from s and p orbitals

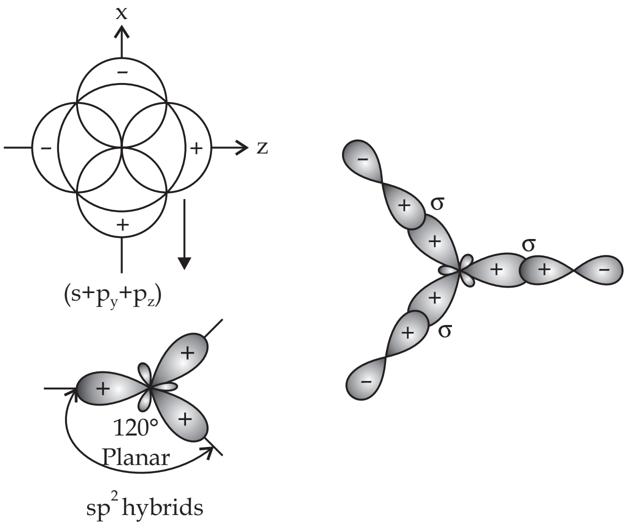


(b) Formation of the linear $BeCl_2$ molecule

(*ii*) **sp^2 hybridisation:** In this type, one *s* and two *p*-orbitals hybridise to form three equivalent sp^2 hybridised orbitals.

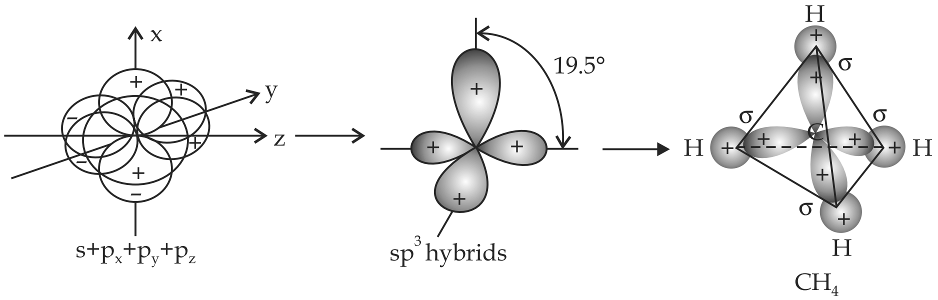
All the three hybrid orbitals remain in the same plane making an angle of 120°.

Example. A few compounds in which sp^2 hybridisation takes place are BF_3, BH_3, BCl_3, carbon compounds containing double bond etc.



Formation of sp^2 hybrids and the BCl_3 molecule

(*iii*) **sp^3 hybridisation:** In this type, one s and three p-orbitals in the valence shell of an atom get hybridised to form four equivalent hybrid orbitals. There is 25% s-character and 75% *p*-character in each sp^3 hybrid orbital. The four sp^3 orbitals are directed towards four corners of the tetrahedron.



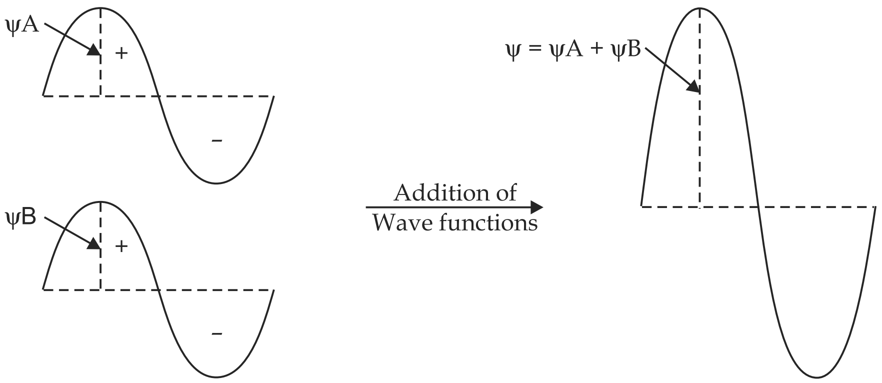
Formation of sp^3 hybrids by the combination of s, p_x, p_y and p_z atomic orbitals of carbon and the formation of CH_4 molecule.

The angle between sp^3 hybrid orbitals is 109.5°.

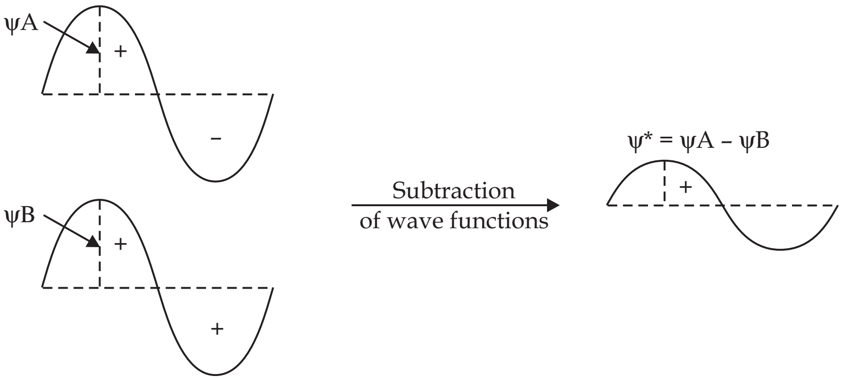
A compound in which sp^3 hybridisation occurs is, (CH_4). The structures of NH_2 and H_2O molecules can also be explained with the help of sp^3 hybridisation.

• Formation of Molecular Orbitals: Linear Combination of Atomic Orbitals (LCAO)

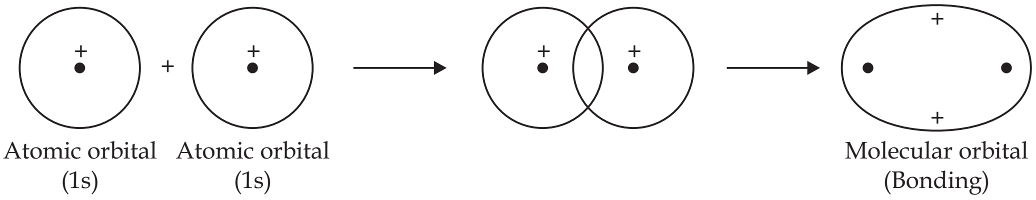
The formation of molecular orbitals can be explained by the linear combination of atomic orbitals. Combination takes place either by addition or by subtraction of wave function as shown below.



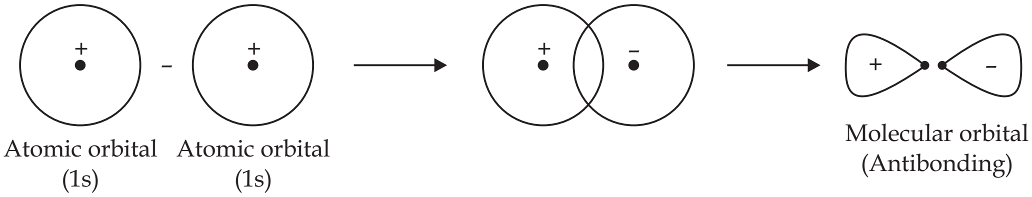
Addition of wave functions



Subtraction of wave functions



Formation of bonding molecular orbital



Formation of antibonding molecular orbital

The molecular orbital formed by addition of atomic orbitals is called bonding molecular orbital while molecular orbital formed by subtraction of atomic orbitals is called antibonding molecular orbital.

Conditions for the combination of atomic orbitals:

(1) The combining atomic orbitals must have almost equal energy.

(2) The combining atomic orbitals must have same symmetry about the molecular axis.

(3) The combining atomic orbitals must overlap to the maximum extent.

• Types of Molecular Orbitals

Sigma (σ) Molecular Orbitals: They are symmetrical around the bond-axis.

pi (π) Molecular Orbitals: They are not symmetrical, because of the presence of positive lobes above and negative lobes below the molecular plane.

• Electronic configuration and Molecular Behaviour

The distribution of electrons among various molecular orbitals is called electronic configuration of the molecule.

• Stability of Molecules

If N_b = No. of electrons occupying bonding orbitals.
N_a = No. of electrons occupying antibonding orbitals.

then

(*i*) If $N_b > N_a$ molecule will be stable.

(*ii*) $N_b < N_a$ molecule will be unstable.

• Bond Order

Bond order is defined as half of the difference between the number of electrons present in bonding and antibonding molecular orbitals.

$$\text{Bond order (B.O.)} = \frac{1}{2}[N_b - N_a]$$

The bond order may be a whole number, a fraction or even zero.

It may also be positive or negative.

Nature of the bond: Integral bond order value for single double and triple bond will be 1, 2 and 3 respectively.

Bond-Length: Bond order is inversely proportional to bond-length. Thus, greater the bond order, smaller will be the bond-length.

Magnetic Nature: If all the molecular orbitals have paired electrons, the substance is diamagnetic. If one or more molecular orbitals have unpaired electrons, it is paramagnetic *e.g.*, O_2 molecule.

Bonding in Some Homonuclear (Diatomic) Molecules

(1) **Hydrogen molecule (H_2):** It is formed by the combination of two hydrogen atoms. Each hydrogen atom has one electron in 1s orbital, so, the electronic configuration of hydrogen molecule is

$$H_2 = (\sigma 1s)^2$$

$$\text{Bond order (B.O.) of } H_2 = \frac{1}{2}(2-0) = 1$$

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

This indicates that two hydrogen atoms are bonded by a single covalent bond.

Bond disssociation energy of hydrogen has been found = 438 kJ/mole.

Bond-Length = 74 pm

No unpaired electron is present therefore, it is diamagnetic.

(2) **Helium molecule (He_2):** Each helium atom contains 2 electrons, thus in He_2 molecule there would be 4 electrons.

The electrons will be accommodated in $\sigma 1s$ and $\sigma^* 1s$ molecular orbitals:

Electronic configuration

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

$$\text{Bond order} = \frac{1}{2}[2-2] = 0$$

He_2 molecule is therefore unstable and does not exist.

(3) **Lithium molecule (Li_2)**

$$\text{E.C. of Li} = 1s^2 2s^1$$

There are 6 electrons in Li_2

$$\text{E.C. of } Li_2 = (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2$$

It can also be represented as KK $[\sigma 2s]^2$

$$\text{Bond order} = \frac{1}{2}[N_b - N_a]$$

$$= \frac{1}{2}[4-2] = 1$$

Nature = Diamagnetic, since molecular orbitals are completely filled.

(4) **Oxygen molecule (O_2)**

The orbital configuration of oxygen is:

$$(Z = 8) = 1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$$

This means that sixteen electrons are to be filled in the molecular orbital of oxygen molecule (O_2).

The molecular orbital configuration

$$= [\sigma 1s]^2 [\sigma^* 1s]^2 [\sigma^* 2s]^2 [\sigma 2p_z]^2 [\pi 2p_x]^2 [\pi 2P_y]^2 [\pi^* 2P_x]^1 [\pi^* 2P_y]^1$$

It may also be written as:

$$KK[\sigma 2s]^2[\sigma * 2s]^2[\sigma 2P_z]^2[\pi 2p_x]^2[\pi 2p_y]^2[\pi * 2P_x]^1[\pi * 2P_y]^1$$

$$B.O. = \frac{1}{2}[N_b - N_a] = \frac{1}{2}[8-4] = 2$$

Nature: Paramagnetic due to the presence of two unpaired electrons.

• Hydrogen Bonding

When highly electronegative elements like nitrogen, oxygen, flourine are attached to hydrogen to form covalent bond, the electrons of the covalent bond are shifted towards the more electronegative atom. Thus, partial positive charge develops on hydrogen atom which forms a bond with the other electronegative atom. This bond is known as hydrogen bond and it is weaker than the covalent bond. For example, in HF molecule, hydrogen bond exists between hydrogen atom of one molecule and fluorine atom of another molecule.

It can be depicted as

$$\cdots\cdots H^{\delta+} - F^{\delta-} \cdots\cdots H^{\delta+} - F^{\delta-} \cdots\cdots H^{\delta+} - F^{\delta-}$$

Hydrogen bond is represented by (– – –) dotted line, while a solid line represents the covalent bond.

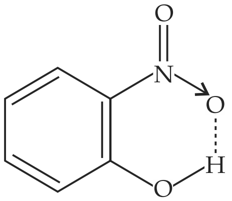
• Types of H-Bonds

(*i*) Intermolecular hydrogen bond

(*ii*) Intramolecular hydrogen bond.

(*i*) **Intermolecular hydrogen bond:** It is formed between two different molecules of the same or different compounds. For Example, in HF molecules, water molecules etc.

(*ii*) **Intramolecular hydrogen bond:** In this type, hydrogen atom is in between the two highly electronegative F, N, O atoms present within the same molecule. For example, in o-nitrophenol, the hydrogen is in between the two oxygen atoms.



Intramolecular hydrogen bonding in o-nitrophenol molecule

NCERT TEXTBOOK QUESTIONS SOLVED

Q1. *Explain the formation of a chemical bond.*

Ans. According to Kössel and Lewis, atoms combine together in order to complete their respective octets so as to acquire the stable inert gas configuration. This can occur in two ways; by transfer of one or more electrons from one atom to other or by sharing of electrons between two or more atoms.

Q2. *Write Lewis dot symbols for atoms of the following elements: Mg, Na, B, O, N, Br.*

Ans. $_{12}\text{Mg} = 2, 8, 2$ $\therefore$ Lewis symbol = $\dot{\text{Mg}}\cdot$

$_{11}\text{Na} = 2, 8, 1$ $\therefore$ Lewis symbol = $\dot{\text{Na}}$

$_{5}\text{B} = 2, 3$ $\therefore$ Lewis symbol = $\cdot\dot{\text{B}}\cdot$

$_{8}\text{O} = 2, 6$ $\therefore$ Lewis symbol = $:\ddot{\text{O}}:$

$_{7}\text{N} = 2, 5$ $\therefore$ Lewis symbol = $:\underset{\cdot}{\dot{\text{N}}}\cdot$

$_{35}\text{Br} = 2, 8, 18, 7$ $\therefore$ Lewis symbol = $:\underset{\cdot\cdot}{\ddot{\text{Br}}}\cdot$

Q3. *Write Lewis symbols for the following atoms and ions: S and* S^{2-}*; Al and* Al^{3+}*; H and* H^-

Ans. $_{16}\text{S} = 2, 8, 6$ $\therefore$ Lewis symbol = $:\ddot{\text{S}}:$, S^{2-} ions = $[:\underset{\cdot\cdot}{\ddot{\text{S}}}:]^{2-}$

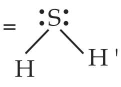
$_{13}\text{Al} = 2, 8, 3$ $\therefore$ Lewis symbol = $\cdot\dot{\text{Al}}\cdot$, Al^{3+} ion = $[\text{Al}]^{3+}$

$_{1}\text{H} = 1$ $\therefore$ Lewis symbol = $\text{H}\cdot$, H^- ion = $\dot{\text{H}}\cdot$

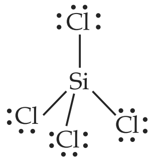
Q4. *Draw the Lewis structures for the following molecules and ions:*
H_2S, $SiCl_4$, BeF_2, CO_3^{2-}, HCOOH

Ans.

H_2S =

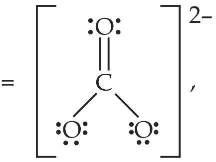


$SiCl_4$ =

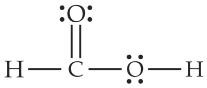


BeF_2 = $:\underset{\cdot\cdot}{\ddot{\text{F}}} - \text{Be} - \underset{\cdot\cdot}{\ddot{\text{F}}}:$

CO_3^{2-} =



HCOOH =



$\text{H} - \overset{\overset{:\text{O}:}{\|}}{\text{C}} - \underset{\cdot\cdot}{\ddot{\text{O}}} - \text{H}$

Q5. *Define Octet rule. Write its significance and limitations.*

Ans. **Octet rule:** Atoms of elements combine with each other in order to complete their respective octets so as to acquire the stable gas configuration.

Significance: It helps to explain why different atoms combine with each other to form ionic compounds or covalent compounds.

Limitations of Octet rule:

(*i*) According to Octet rule, atoms take part in chemical combination to achieve the configuration of nearest noble gas elements. However, some of noble gas elements like Xenon have formed compounds with fluorine and oxygen. For example: XeF_2, XeF_4 etc.

Therefore, validity of the octet rule has been challenged.

(*ii*) This theory does not account for shape of molecules.

Q6. *Write the favourable factors for the formation of ionic bond.*

Ans. (*i*) Low ionization enthalpy of metal atoms

(*ii*) High electron gain enthalpy of non-metal atoms

(*iii*) High lattice enthalpy of compound formed.

Q7. *Discuss the shape of the following molecules using the VSEPR model:*
$BeCl_2$, BCl_3, $SiCl_4$, AsF_5, H_2S, PH_3

Ans. (*i*) $BeCl_2 = Cl\!:\ Be\!:\ Cl$.

The central atom has only two bond pairs and there is no lone pair, *i.e.,* it is of the type AB_2. Hence, shape is **linear.**

(*ii*) $BCl_3 = Cl\ :\ddot{B}\!:\ Cl$.

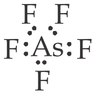
The central atom has only 3 bond pairs and no lone pair, *i.e.,* it is of the type AB_3. Hence, shape is **triangular planar.**

(*iii*) $SiCl_4$ =

$$\begin{matrix} & Cl & \\ Cl\!: & \underset{..}{\overset{..}{Si}} & \!:Cl \\ & Cl & \end{matrix}$$

Bond pairs = 4, lone pairs = 0, *i.e.,* it is of the type AB_4.
Hence, shape is **Tetrahedral.**

(*iv*) AsF_5 =



$$\begin{matrix} & F\ \ F & \\ F\!: & \underset{..}{\overset{..\ ..}{As}} & \!:F \\ & F & \end{matrix}$$

Bond pairs = 5, lone pairs = 0, *i.e.,* it is of the type AB_5.
Hence, shape is **Trigonal bipyramidal.**

(*v*) $H_2S = H\!:\underset{..}{\ddot{S}}\!:H$

Bond pairs = 2, lone pairs = 2, *i.e.,* it is of the type AB_2L_2.
Hence, shape is **Bent/V-shaped.**

(*vi*) PH_3 =

$$\begin{matrix} & H & \\ H\!: & \underset{..}{\overset{..}{P}} & \!:H \end{matrix}$$

Bond pairs = 3, lone pair = 1, *i.e.,* it is of the type AB_3L.

Hence, shape is **Trigonal.**

Q8. *Although geometries of* NH_3 *and* H_2O *molecules are distorted tetrahedral, bond angle in water is less than that of ammonia. Discuss.*

Ans. $NH_3 \rightarrow \ddot{N}H_3$

$H_2O \rightarrow H_2\ddot{O}\!:$

Because of two lone pairs of electrons on O-atom, repulsion on bond pairs is greater in H_2O in comparison to NH_3. Thus, the bond angle is less in H_2O molecules.

Q9. *How do you express the bond strength in terms of bond order?*

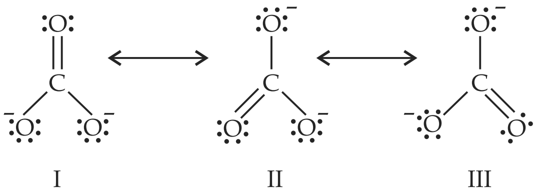
Ans. Bond strength is directly proportional to the bond order. Greater the bond order, more is the bond strength.

Q10. *Define the bond-length.*

Ans. **Bond-length:** It is the equilibrium distance between the nuclei of two bonded atoms in a molecule. Bond-lengths are measured by spectroscopic methods.

Q11. *Explain the important aspects of resonance with reference to the* CO_3^{2-} *ion.*

Ans.



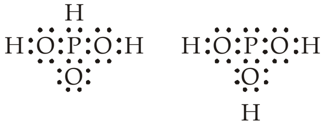
Resonance in CO_3^{2-}*, I, II and III represent the three canonical forms.*

(*i*) In these structures, the position of nuclei are same.

(*ii*) All the three forms have almost equal energy.

(*iii*) Same number of paired and unpaired electrons, they differ only in their position.

Q12. 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.*



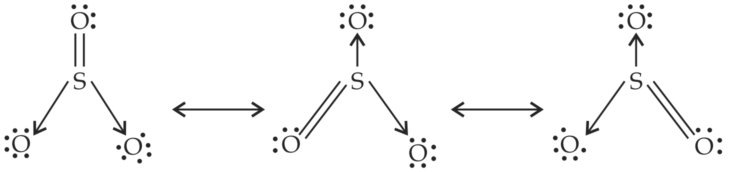
(1) (2)

Ans. No, these cannot be taken as canonical forms because the positions of atoms have been changed.

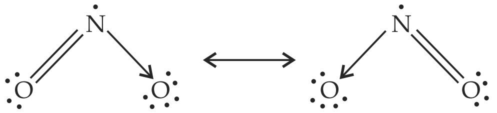
Q13. *Write the resonance structures for* SO_3*,* NO_2 *and* NO_3^-

Ans.

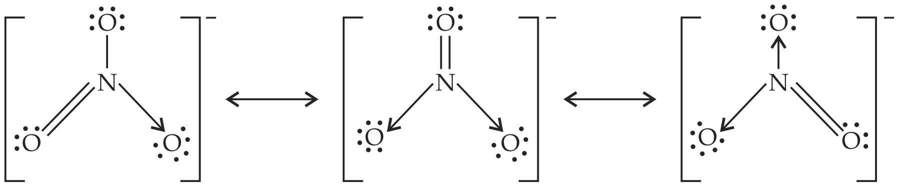
SO_3:



NO_2:

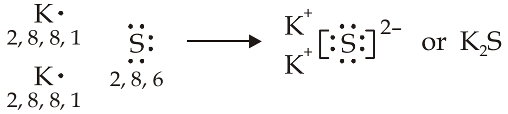


NO_3^-:



Q14. *Use Lewis symbols to show electron transfer between the following atoms to form cations and anions (a) K and S (b) Ca and O (c) Al and N.*

Ans. (*a*)



(*b*) $\underset{2,8,8,2}{\text{Ca}:} + \underset{2,6}{\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{O}}}:} \longrightarrow \text{Ca}^{2+}[:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{O}}}:] \text{ or } \text{Ca}^{2+}\text{O}^{2-}$

(*c*) $\underset{2,8,3}{\text{Al}:} \quad \underset{2,5}{\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{N}}}:} \longrightarrow \text{Al}^{3+}[:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{N}}}:] \text{ or } \text{Al}^{3+}\text{N}^{3-}$

Q15. *Although both CO_2 and H_2O are triatomic molecules, the shape of H_2O molecule is bent while that of CO_2 is linear. Explain this on the basis of dipole moment.*

Ans. In CO_2, there are two C=O bonds. Each C=O bond is a polar bond.

The net dipole moment of CO_2 molecule is zero. This is possible only if CO_2 is a linear molecule. (O=C=O). The bond dipoles of two C=O bonds cancel the moment of each other.

Whereas, H_2O molecule has a net dipole moment (1.84 D). H_2O molecule has a bent structure because here the O—H bonds are oriented at an angle of 104.5° and do not cancel the bond moments of each other.

Q16. *Write the significance/applications of dipole moment.*

Ans. (*i*) **In predicting the nature of the molecules:** Molecules with specific dipole moments are polar in nature and those of zero dipole moments are non-polar in nature.

(*ii*) In the determination of shapes of molecules.

(*iii*) In calculating the percentage ionic character.

Q17. *Define electronegativity. How does it differ from electron gain enthalpy?*

Ans. **Electronegativity:** Electronegativity is the tendency of an atom to attract shared pair of electrons. It is the property of bonded atom.

Whereas, electron gain enthalpy is the tendency of an atom to attract outside electron. It is the property of an isolated atom.

Q18. *Explain with the help of suitable example polar covalent bond.*

Ans. When two atoms with different electronegativity are linked to each other by covalent bond, the shared electron pair will not in the centre because of the difference in electronegativity. For example, in hydrogen flouride molecule, flouride has greater electronegativity than hydrogen. Thus, the shared electron pair is displaced more towards flourine atom, the later will acquire a partial negative charge (δ^-). At the same time hydrogen atom will have a partial positive charge (δ^+). Such a covalent bond is known as polar covalent bond or simply polar bond.

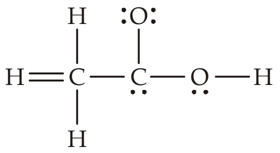
It is represented as

$$\overset{\delta^+}{\underset{(2.1)}{\text{H}}} - \overset{\delta^-}{\underset{(4.0)}{\text{F}}}$$

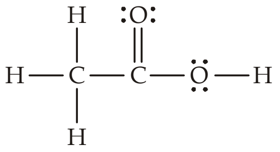
Q19. *Arrange the bonds in order of increasing ionic character in the molecules: LiF, K_2O, N_2, SO_2 and ClF_3.*

Ans. $N_2 < SO_2 < ClF_3 < K_2O < LiF$

Q20. *The skeletal structure of CH_3COOH as shown below is correct, but some of the bonds are shown incorrectly. Write the correct Lewis structure for acetic acid.*



Ans.



Q21. *Apart from tetrahedral geometry, another possible geometry for CH_4 is square planar with the four H atoms at the corners of the square and the C atom at its centre. Explain why CH_4 is not square planar?*

Ans. According to VSEPR theory, if CH_4 were square planar, the bond angle would be 90°. For tetrahedral structure, the bond angle is 109°28'. Therefore, in square planar structure, repulsion between bond pairs would be more and thus the stability will be less.

Q22. *Explain why BeH_2 molecule has a zero dipole moment although the Be—H bonds are polar.*

Ans. BeH_2 is a linear molecular (H—Be—H), the bond angle = 180°.

Be—H bonds are polar due to difference in their electronegativity but the bond polarities cancel each other. Thus, molecule has resultant dipole moment of zero.

Q23. *Which out of NH_3 and NF_3 has higher dipole moment and why?*

Ans. In NH_3 and NF_3, the difference in electronegativity is nearly same but the dipole moment of NH_3 = (1.46D)

For Example, NF_3 = (0.24D)

In NH_3, the dipole moments of the three N—H bonds are in the same direction as the lone pair of electron. But in NF_3, the dipole moments of the three N—F bonds are in the direction opposite to that of the lone pair. Therefore, the resultant dipole moment in NH_3 is more than in NF_3.

Q24. *What is meant by hybridisation of atomic orbitals? Describe the shapes of sp, sp^2, sp^3 hybrid orbitals.*

Ans. **Hybridisation:** It is defined as the process of intermixing of atomic oribitals of slightly different energies to give rise to new hybridized orbitals having equivalent energy and identical shapes.

Shapes of Orbitals:

sp hybridisation: When one *s*-and one *p*-orbital, intermix then it is called sp-hybridisation. For example, in BeF_2, Be atom undergoes sp-hybridisation. It has linear shape. Bond angle is 180°.

sp^2 hybridisation: One *s*-and two *p*-orbitals get hybridised to form three equivalent hybrid orbitals. The three hybrid orbitals directed towards three corners of an equilateral triangle. It is, therefore, known as trigonal hybridisation.

sp^3 hybridisation: One *s*-and three *p*-orbitals get hybridised to form four equivalent hybrid orbitals. These orbitals are directed towards the four corners of a regular tetrahedron.

Q25. *Describe the change in hybridisation (if any) of the Al atom in the following reaction.*

$$AlCl_3 + Cl^- \longrightarrow AlCl_4^-$$

Ans. Electronic configuration of $_{13}Al = 1s^2\,2s^2\,2p^6\,3s^1\,3p_x^{\,1}\,3p_y^{\,1}$
(excited state)

Hence, hybridisation will be sp^2

In $AlCl_4^-$, the empty $3p_z$ orbital is also involved. So, the hybridisation is sp^3 and the shape is tetrahedral.

Q26. *Is there any change in the hybridisation of B and N atoms as a result of the following reaction?*

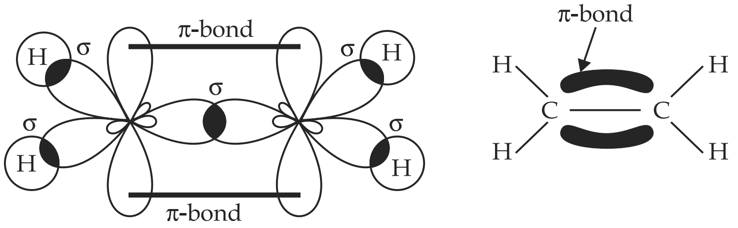
$$BF_3 + NH_3 \longrightarrow F_3\,B.NH_3$$

Ans. In BF_3, B atom is sp^2 hybridised. In NH_3, N is sp^3 hybridised.

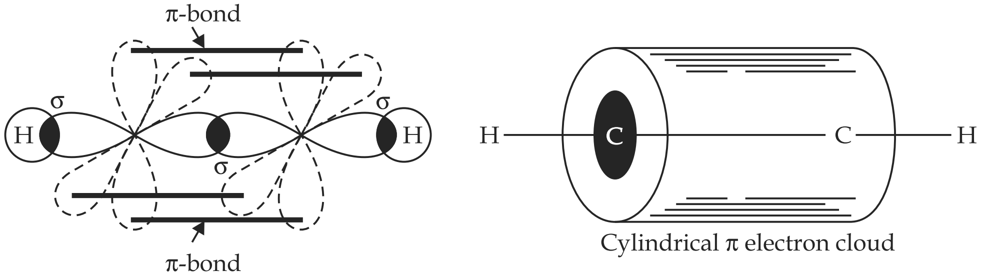
After the reaction, hybridisation of B changes from sp^2 to sp^3.

Q27. *Draw diagrams showing the formation of a double bond and a triple bond between carbon atoms in C_2H_4 and C_2H_2 molecules.*

Ans.



Oribital picture of ethene molecule



Oribital picture of ethyne molecule

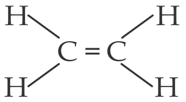
Q28. *What is the total number of sigma and pi bonds in the following molecules?*

(a) C_2H_2 *(b)* C_2H_4

Ans. (*a*) $H-C\equiv C-H$

Sigma bond = 3

π bonds = 2

(*b*) 

Sigma bond = 5

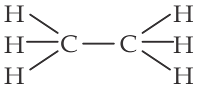
π bonds = 1

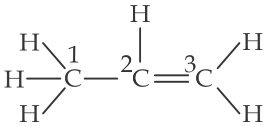
Q29. *Considering X-axis as the internuclear axis which out of the following will not form a sigma bond and why? (a) 1s and 1s (b) 1s and $2p_x$ (c) $2p_y$ and $2p_y$ (d) 1s and 2s*

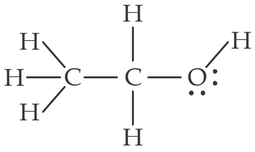
Ans. (*c*) It will not form a *s*-bond because taking x-axis as the internuclear axis, there will be lateral overlap between the two $2p_y$ orbitals forming a π-bond.

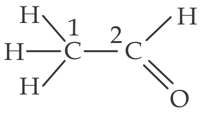
Q30. *Which hybrid orbitals are used by carbon atoms in the following molecules?*

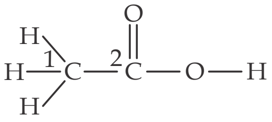
(a) CH_3-CH_3 *(b)* $CH_3-CH=CH_2$ *(c)* CH_3-CH_2-OH *(d)* CH_3-CHO *(e)* CH_3COOH.

Ans. (*a*)  Both C−atoms use sp^3 hybrid orbitals.

(*b*)  $C_1 = sp^3$, $C_2 = sp^2$, $C_3 = sp^2$

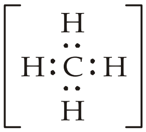
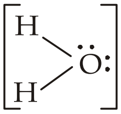
(*c*)  Both C−atoms use sp^3 hybrid orbitals.

(*d*)  $C_1 = sp^3$, $C_2 = sp^2$

(*e*)  $C_1 = sp^3$, $C_2 = sp^2$

Q31. *What do you understand by bond pairs and lone pairs of electrons? Illustrate by giving one example of each type.*

Ans. The electron pair involved in sharing between two atoms during covalent bonding is called shared pair or bond pair. At the same time, the electron pair which is not involved in sharing is called lone pair of electrons.

For Example, In CH_4,  there are only 4 bond pairs, but in H_2O, 

there are two bond pairs and two lone pairs.

Q32. *Distinguish between a sigma bond and a pi bond.*

Ans.

Sigma (σ) Bond	*pi (π) Bond*
(1) σ-bond is formed by the axial overlap of the atomic orbitals.	(1) π-bond is formed by the sidewise overlap of atomic orbitals.
(2) The bond is quite strong.	(2) Comparatively weak bond.
(3) Only one lobe of the p-orbitals is involved in the overlap.	(3) Both lobes of the p-orbitals are involved in the overlap.
(4) Electron cloud of the molecular orbital is symmetrical around the internuclear axis.	(4) The electron cloud is not symmetrical.

Q33. *Explain the formation of H_2 molecule on the basis of valence bond theory.*

Ans. Let us consider the combination between atoms of hydrogen H_A and H_B and e_A and e_B be their respective electrons.

As they tend to come closer, two different forces operate between the nucleus and the electron of the other and vice versa. The nuclei of the atoms as well as their electrons repel each other. Energy is needed to overcome the force of repulsion. Although the number of new attractive and repulsive forces is the same, but the magnitude of the attractive forces is more. Thus, when two hydrogen atoms approach each other, the overall potential energy of the system decreases. Thus, a stable molecule of hydrogen is formed.

Q34. *Write the important conditions required for the linear combination of atomic orbitals to form molecular orbitals.*

Ans. (*i*) The combining atomic orbitals should have comparable energies.

For example, 1s orbital of one atom can combine with 1s atomic orbital of another atom, 2s can combine with 2s.

(*ii*) The combining atomic orbitals must have proper orientations. So that they are able to overlap to a considerable extent.

(*iii*) The extent of overlapping should be large.

Q35. *Use molecular orbital theory to explain why the Be_2 molecule does not exist.*

Ans.

$$\begin{aligned} \text{E.C. of Be} &= 1s^2\,2s^2 \\ \text{M.O.E.C. of Be}_2 &= \sigma^2 1s\ \sigma^{*2} 1s\ \sigma^2 2s\ \sigma^{*2} 2s \\ \text{Bond order} &= \frac{1}{2}(4-4) \\ &= 0 \end{aligned}$$

Hence, Be_2 does not exist.

Q36. *Compare the relative stability of the following species and indicate their magnetic properties: O_2, O_2^+, O_2^- (Superoxide), O_2^{2-} (peroxide)*

Ans.

O_2 — Bond order = 2, paramagnetic

O_2^+ — Bond order = 2.5, paramagnetic

O_2^- — Bond order = 1.5, paramagnetic

O_2^{2-} — Bond order = 1, diamagnetic

Order of relative stability is

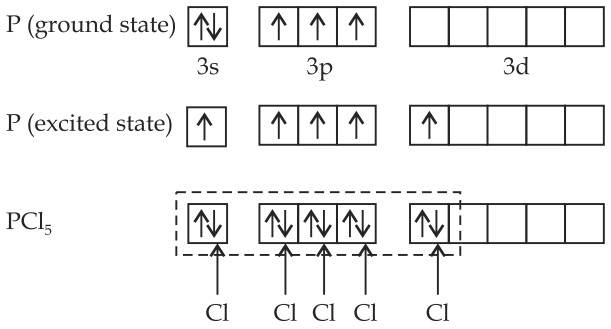
$$\underset{(2.5)}{O_2^+} > \underset{(2.0)}{O_2} > \underset{(1.5)}{O_2^-} > \underset{(1.0)}{O_2^{2-}}$$

Q37. *Write the significance of plus and minus sign in representing the orbitals.*

Ans. Plus and minus sign is used to indentify the nature of electrons wave. Plus (+ve) sign denotes crest, while (–ve) sign denotes trough.

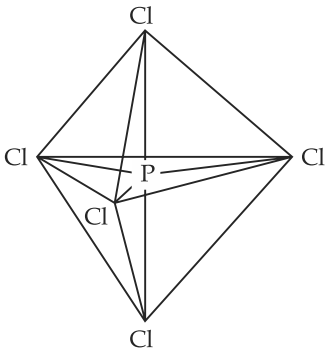
Q38. *Describe the hybridisation in case of PCl_5. Why are the axial bonds longer as compared to equatorial bonds?*

Ans. The ground state E.C. and the excited state E.C. of phosphorus are represented as:



sp^3 hybrid orbitals filled by electron pairs donated by five Cl atoms

The one s, three-p and one d-orbitals hybridise to yield five sets of sp^3d hybrid orbitals which are directed towards the five corners of a trigonal bipyramidal as in Fig.



Trigonal bipyramidal geometry of PCl_5 molecule

Because axial bond pairs suffer more repulsive interaction from the equatorial bond pairs, therefore axial bonds have been found to be slightly longer and hence slightly weaker than equatorial bonds.

Q39. *Define hydrogen bonds. Is it weaker or stronger than the van der Waals forces?*

Ans. When hydrogen is attached with highly electronegative element in a covalent bonding the electrons of the covalent bond are shifted towards the more electronegative atom. Thus, partially positively charged hydrogen atom forms a bond with the other more electronegative atom. This bond is known as hydrogen bond. Hydrogen bond is stronger than the van der Waals forces.

Q40. *What is meant by the term bond order? Calculate the bond order of:*

N_2, O_2, O_2^+, O_2^-

Ans. Bond order is defined as the half of the difference between the number of electrons present in bonding and antibonding molecular orbitals.

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

$$\text{E.C of } N_2 = 1s^2\, 2s^2\, 2p_x^{\,1} 2p_y^{\,1} 2p_z^{\,1}$$

(*i*) M.O. configuration of $N_2 = [\sigma 1s]^2[\sigma^* 1s]^2[\sigma 2s]^2[\sigma^* 2s]^2[\pi 2p_x]^2[\pi 2p_y]^2[\sigma 2p_z]^2$

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

$$= \frac{1}{2}[8-2] = 3$$

(*ii*) M.O. configuration of $O_2 = [\sigma 1s]^2[\sigma^* 1s]^2[\sigma 2s]^2[\sigma^* 2s]^2[\sigma 2p_z]^2$

$$\text{B.O} = \frac{1}{2}[N_b - N_a]$$

$$= \frac{1}{2}[8-4] = 2$$

(*iii*) M.O. configuration of $O_2^+ = KK[\sigma 2s]^2\, [\sigma^* 2s]^2\, [\sigma 2p_z]^2\, [\pi 2p_x]^2\, [\pi 2p_y]^2\, [\pi^* 2p_x]^1$

$$\text{B.O.} = \frac{1}{2}[8-3] = 2.5$$

(*iv*) M.O. configuration of O_2^-

$$= KK[\sigma 2s]^2\, [\sigma^* 2s]^2\, [\sigma 2p_z]^2\, [\pi 2p_x]^2\, [\pi 2p_y]^2\, [\pi^* 2p_x]^2\, [\pi^* 2p_y]^1$$

$$\text{B.O.} = \frac{1}{2}[8-5] = 1.5$$

MORE QUESTIONS SOLVED

I. VERY SHORT ANSWER TYPE QUESTIONS

Q1. *How is bond order related to the stability of a molecule?*

Ans. Higher the bond order, greater is the stability.

Q2. *Write the type of hybridisation involved in CH_4, C_2H_4 and C_2H_2.*

Ans.
CH_4 = sp^3
C_2H_4 = sp^2
C_2H_2 = sp

Q3. *Out of σ and π bonds, which one is stronger and why?*

Ans. σ-bond is stronger. This is because σ-bond is formed by head-on overlapping of atomic orbitals and π bond is formed by sidewise overlapping.

Q4. *Write the Lewis dot symbols of the following elements and predict their valencies.*

(i) Cl (ii) P

Ans. (*i*) $:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}\cdot$

(valency = 8 – 7 = 1)

(*ii*) $\cdot\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{P}}}$

(valency = 8 – 5 = 3)

Q5. *Predict the shapes of the following molecules using VSEPR theory?*

(i) $BeCl_2$ *(ii)* $SiCl_4$

Ans. (*i*) Linear

(*ii*) Tetrahedral

Q6. *Write the state of hybridisation of boron in* BF_3.

Ans. sp^2.

Q7. *Arrange* O_2, O_2^-, O_2^{2-}, O_2^+ *in increasing order of bond energy.*

Ans. $O_2^{2-} < O_2^- < O_2 < O_2^+$

Q8. *What is meant by bond pairs of electrons?*

Ans. The electron pairs involved in the bond formation are known as bond pairs or shared pairs.

Q9. *Which of the following has larger bond angle in each pair?*

(i) CO_2, BF_3 *(ii)* NH_3, CH_4

Ans. (*i*) CO_2 (*ii*) CH_4

Q10. *Arrange the following, according to increasing covalent nature.*

$NaCl$, $MgCl_2$, $AlCl_3$

Ans. $NaCl < MgCl_2 < AlCl_3$

Q11. *Define covalent bond according to orbital concept?*

Ans. Covalent bond can be formed by the overlap of the orbitals belonging to the two atoms having opposite spins of electrons.

Q12. *Why* B_2 *is paramagnetic in nature while* C_2 *is not?*

Ans. The molecular orbital electronic configuration of both B_2 and C_2 are.

$$B_2: [\sigma 1s]^2[\sigma^* 1s]^2[\sigma 2s]^2[\sigma^* 2s]^2[\pi 2p_x]^1[\pi 2p_y]^1$$

$$C_2: [\sigma 1s]^2[\sigma^* 1s]^2[\sigma 2s]^2[\sigma^* 2s]^2[\pi 2p_x]^2[\pi 2p_y]^2$$

Since, B_2 has two unpaired electrons, B_2 is paramagnetic.

C_2 has no unpaired electron. Thus, C_2 is diamagnetic.

Q13. *Why ethyl alcohol is completely miscible with water?*

Ans. This is because ethyl alcohol forms H-bonds with water.

Q14. *Which is more polar – CO_2 or N_2O? Give reason.*

Ans. N_2O is more polar than CO_2.

This is because CO_2 is linear and symmetrical. Its net dipole moment is zero.

N_2O is linear but not symmetrical. It has a net dipole moment of σ116D.

Q15. *State the types of hybrid orbitals associated with (i) P in PCl_5 and (ii) S in SF_6*

Ans. (*i*) sp^3d of P in PCl_5

(*ii*) sp^3d^2 of S in SF_6

Q16. *Why N_2 is more stable than O_2? Explain on the basis of molecular orbital theory.*

Ans. Bond order of N_2 (= 3) is greater than that of O_2 (= 2).

Q17. *How is bond order related to bond length of a molecule?*

Ans. Bond length is inversely proportional to bond order.

Q18. *Out of bonding and antibonding molecular orbitals, which one has lower energy and which one has higher stability?*

Ans. Bonding molecular orbital has lower energy and higher stability.

Q19. *Define antibonding molecular orbital.*

Ans. The molecular orbital formed by the subtractive effect of the electron waves of the combining atomic orbitals, is called antibonding molecular orbital.

Q20. *Name the two conditions which must be satisfied for hydrogen bonding to take place in a molecule.*

Ans. (*i*) The molecule should contain highly electronegative atom like hydrogen atom.

(*ii*) The size of electronegative atom should be small.

II. SHORT ANSWER TYPE QUESTIONS

Q1. *What is an electrovalent (or ionic) bond? Explain its formation with two examples.*

Ans. When a chemical bond is formed by the complete transfer of electrons from one atom to another, so as to complete their outermost shell and therefore, aquire the stable noble gas configuration, the bond formed is called ionic bond or electrovalent bond.

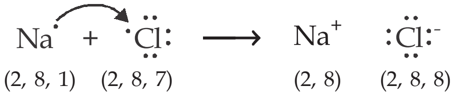
For Example,

(*i*) Formation of sodium chloride (NaCl)

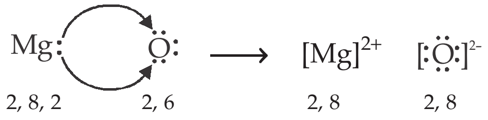
$$\underset{2,\,8,\,1}{Na} \longrightarrow \underset{2,\,8}{Na^+} + e^-$$

$$\underset{2,\,8,\,7}{Cl} + e^- \longrightarrow \underset{2,\,8,\,8}{[Cl]^-}$$

$$Na^+ + Cl^- \longrightarrow [Na^+]\,[Cl]^-$$



(*ii*) Formation of magnesium oxide (MgO)



or MgO

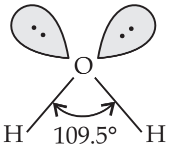
Q2. *What are Lewis structures? Write the Lewis structure of H_2, BeF_2 and H_2O.*

Ans. The outer shell electrons are shown as dots surrounding the symbol of the atom. These symbols are known as Lewis symbols or Lewis structures.

H_2 – H : H

BeF_2 – $:\ddot{\underset{\cdot\cdot}{F}}:Be:\ddot{\underset{\cdot\cdot}{F}}:$

H_2O –



Q3. *Define Lattice energy. How is Lattice energy influenced by (i) Charge on the ions (ii) Size of the ions?*

Ans. Lattice energy is defined as the energy released when one mole of crystalline solid is formed by the combination of oppositely charged ions.

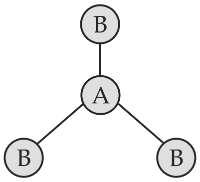
(*i*) As the magnitude of charge on an ion increases there will be greater force of interionic attraction and hence greater will be the value of Lattice energy.

(*ii*) Smaller the size of the ions, lower will be the internuclear distance and thus greater will be the Lattice energy.

Q4. *Give the shapes of the following molecules:*

(i) AB_3 (ii) AB_4

Ans. (*i*)



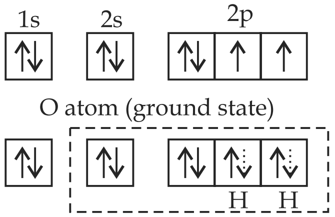
Triangular planar

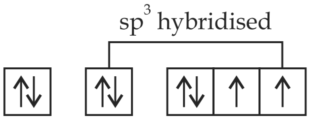
(*ii*) AB_4 – Tetrahedral

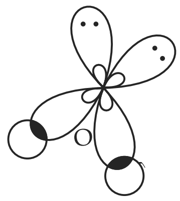
Q5. *Define Hybridisation. Explain sp^3 hybridisation with suitable example.*

Ans. **Hybridisation:** It is the phenomenon of intermixing of atomic orbitals of slightly different energies to form new hybrid orbitals of equivalent energy.

Formation of water. In water (H_2O), the atomic number of oxygen is 8 and its orbitals electronic configuration is $1s^2\,2s^2\,2p_x^2\,2p_y^1\,2p_z^1$. The oxygen atom is also sp^3 hybridised. However, in this case, the two orbitals with one electron each (half filled) are involved in overlap with the hydrogen orbitals.







Orbital picture of H_2O molecule

Q6. *Account for the following:*

(*i*) *Water is a liquid while H_2S is a gas*

(*ii*) *NH_3 has higher boiling point than PH_3.*

Ans. (*i*) In case of water hydrogen bonding causes association of the H_2O molecules. There is no such hydrogen bonding in H_2S, that's why it is a gas.

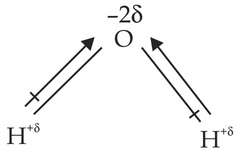
(*ii*) There is hydrogen bonding in NH_3 but not in PH_3.

Q7. *What do you mean by Dipole moment? Draw the dipole diagram of H_2O.*

Ans. The product of magnitude of charges (+ve, or –ve) and distance between them is called dipole moment. It is usually denoted by μ.

$$\mu = Q \times d$$

Its Sl unit is Debye.



$\mu = 1.84$ D

Q8. *What are the main postulates of Valence Shell Electron Pair Repulsion (VSEPR) theory?*

Ans. (*i*) The shape of a molecule depends upon the no. of electron pairs around the central atom.

(*ii*) There is a repulsive force between the electron pairs, which tend to repel one another.

(*iii*) The electron pairs in space tend to occupy such positions that they are at maximum distance so, that the repulsive force will be minimum.

(*iv*) A multiple bond is treated as if it is single bond and the remaining electron pairs which constitute the bond may be regarded as single super pair.

Q9. *Define bond order. How is it related to the stability of a molecule?*

Ans. Bond order is defined as half of the difference between the number of electrons present in bonding and antibonding molecular orbitals.

$$\text{Bond order (B.O.)} = \frac{1}{2}\left[N_b - N_a\right]$$

If the bond order is positive ($N_b > N_a$), the molecule or ion will be stable. If it is negative ($N_b < N_a$) the molecule or ion will be unstable.

Q10. *Explain the diamagnetic behaviour of F_2 molecule on the basis of molecular orbital theory.*

Ans. The orbital electronic configuration of fluorine (Z = 9)

$$= 1s^2\, 2s^2\, 2p_x^2\, 2p_y^2\, 2p_z^1$$

$$\text{M.O.E.C. of fluorine} = \left[\sigma 2s\right]^2 \left[\sigma * 2s\right]^2 \left[\sigma 2p_z\right]^2 \left[\pi^2 p_x\right]^2 \left[\pi 2p_y\right]^2 \left[\pi * 2p_x\right]^2 \left[\pi * 2p_y\right]^2$$

Due to presence of all filled orbitals, F_2 is diamagnetic.

III. LONG ANSWER TYPE QUESTIONS

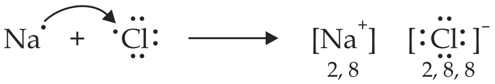
Q1. (a) *Explain the formation of ionic bond with two examples.*

(b) *Discuss the conditions which favour the formation of ionic bond.*

Ans. (*a*) An ionic or electrovalent bond is formed by the complete transferrence of one or more electrons from one atom to another.

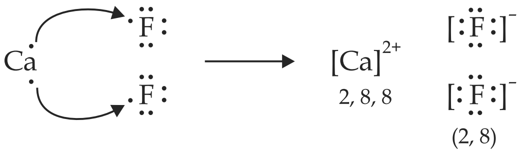
Examples:

(*i*) **Formation of (NaCl)**



or NaCl

(*ii*) **Formation of (CaF_2)**



or CaF_2

(*b*) **Conditions favourable for the formation of ionic bond:**

(*i*) Lesser the ionization enthalpy, easier will be the removal of an electron i.e., formation of a positive ion and hence greater the chances of formation of ionic bond.

(*ii*) Higher is the electron affinity, more is the energy released and stabler will be the negative ion produced. Consequently, the probability of formation of ionic bond will be enhanced.

Q2. (a) *Define dipole moment. What are the units of dipole moment?*

(b) *Dipole moment values help in predicting the shapes of covalent molecules. Explain.*

Ans. (*a*) **Dipole moment:** In a polar molecule, one end bears a positive charge and the other has a negative charge. Thus, the molecule has two poles with equal magnitude of the charges. The molecule is known as dipolar molecule and possesses dipole moment.

It is defined as the product of the magnitude of the positive or negative charge and the distance between the charges.

$$\mu \text{ (dipole moment)} = q \times d$$

SI unit of dipole moment is coulomb metre (m) or Debye.

(*b*) The dipole moment values are quite helpful in determining the general shapes of molecules.

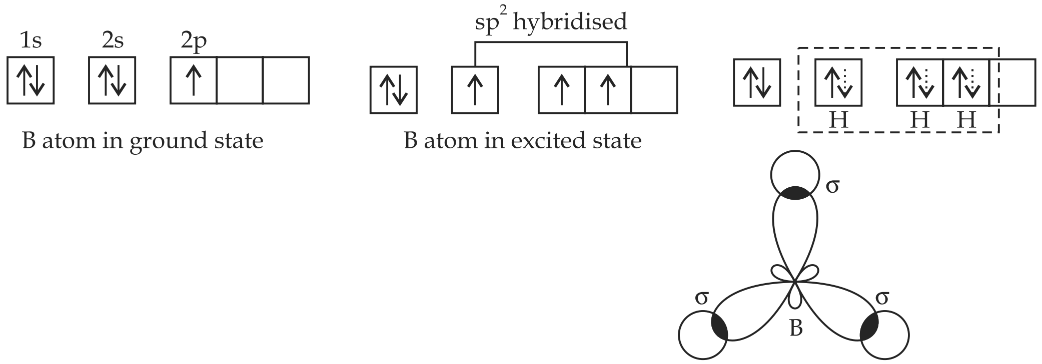
For molecules with zero dipole moment, shapes will be either linear or symmetrical.

For Example. BeF_2, CO_2 etc.

Molecules that possess dipole moments, their shape will not be symmetrical.

Q3. *Discuss the orbital structures of the following molecules on the basis of hybridisation.*
(i) BH_3 *(ii)* C_2H_2

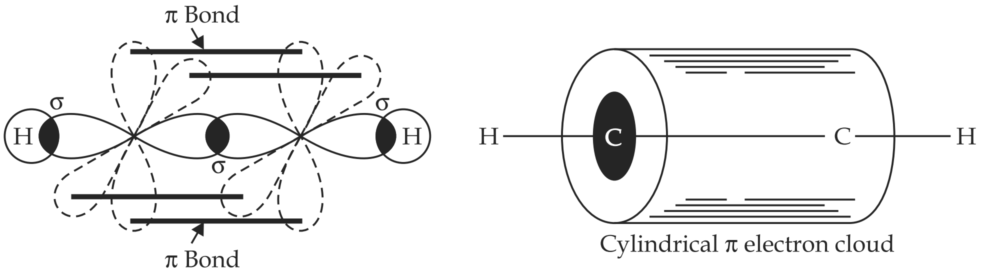
Ans. (*i*) **Formation of BH_3** (atomic No. of B is 5.)



Orbital picture of BH_3 molecule

B atom gets hybridised to form three equivalent hybrid orbitals directed towards three corners of equilateral triangle with B atoms in the centre. Bond angle = 120°.

(*ii*) **C_2H_2**



Orbital picture of ethyne

Both the carbon atoms are sp hybridised. Both the carbon atoms have also two unhybridised orbitals which overlap sidewise with the similar orbitals of the other carbon atom to form two π bonds.

Q4. *(a) How many σ and π bonds are present in*

$$CH_2{=}CH-C{\equiv}CH$$

(b) Why H_2^+ *is more stable than* H_2^-*?*

(c) Why is B_2 *molecule paramagnetic?*

Ans. (*a*) No. of σ bonds = 7

No. of π bonds = 3

(*b*) Both the ions have the same bond order (0.5) but they differ in their configuration.

H_2^+ ion = $[\sigma 1s]^1$,

H_2^- ion = $[\sigma 1s]^2\,[\sigma^* 1s]^1$

Since, H_2^- ion has an electron in the antibonding molecular orbital, it is therefore less stable.

(*c*) The molecular orbital configuration of B_2 is given

B_2: $[\sigma 1s]^2[\sigma^* 1s]^2[\sigma 2s]^2[\sigma^* 2s]^2[\pi 2p_x]^1[\pi^* 2p_y]^1$

Since, B_2 has two unpaired electrons, it is paramagnetic.

IV. MULTIPLE CHOICE QUESTIONS

1. A co-ordinate bond is formed by:

(*a*) sharing of electrons contributed by both the atoms
(*b*) complete transfer of electrons
(*c*) sharing of electrons contributed by one atom only
(*d*) none of these

2. The species CO, CN^- and N_2 are:

(*a*) isoelectronic (*b*) having coordinated bond
(*c*) having polar bond (*d*) having low bond energies

3. The axial overlap between the two orbitals leads to the formation of a:

(*a*) sigma bond (*b*) pi bond (*c*) multiple bond (*d*) none of these

4. In SO_2 molecule, S atom is:

(*a*) sp^3 hybridized (*b*) sp hybridized (*c*) sp^2 hybridized (*d*) *d* sp^2 hybridized

5. A molecule or ion is stable if:

(*a*) $N_b = N_a$ (*b*) $N_b < N_a$ (*c*) $N_a < N_b$ (*d*) $N_a - N_b = +$ ve

6. The molecule Ne_2 does not exist because

(*a*) $N_b > N_a$ (*b*) $N_b = N_a$ (*c*) $N_b < N_a$ (*d*) None of these

7. Which one is diamagnetic among NO^+, NO and NO^-?

(*a*) NO^+ (*b*) NO (*c*) NO^- (*d*) None of these

8. In sp^3, sp^2 and sp hybridized carbon atom, the *p* character is maximum in:

(*a*) sp^3 (*b*) sp^2
(*c*) sp (*d*) all of the above have same *p*-character

9. Out of the following, intramolecular hydrogen bonding exists in:

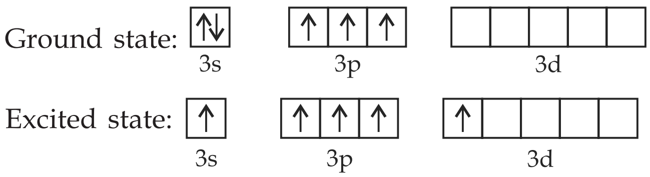
(*a*) water (*b*) H_2S (*c*) 4-nitrophenol (*d*) 2-nitrophenol

Ans. 1. (*c*) 2. (*a*) 3. (*a*) 4. (*c*) 5. (*c*)
6. (*b*) 7. (*a*) 8. (*a*) 9. (*d*)

V. HOTS QUESTIONS

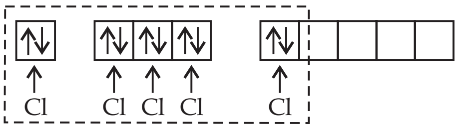
Q1. *Describe the hybridisation in case of PCl_5. Why are the axial bonds longer as compared to equatorial bonds?*

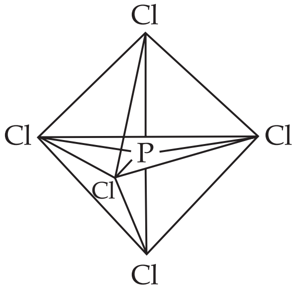
Ans. The ground state and excited state outer electronic configurations of phosphorus (Z = 15) are:



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

PCl_5





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

There are five P–Cl sigma bonds in PCl_5. Three P–Cl bonds lie in one plane and make an angle of 120° with each other. These bonds are called equatorial bonds. The remaining two P–Cl bonds lie above and below the equatorial plane and make an angle of 90° with the plane. These bonds are called axial bonds.

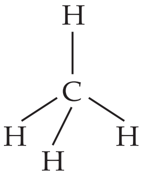
As the axial bond pairs suffer more repulsion from the equatorial bond pairs, axial bonds are slightly longer than equatorial bonds.

Q2. *Apart from tetrahedral geometry, another possible geometry for CH_4 is square planar with the four H atoms at the corners of the square and the C atoms at its centre. Explain why CH_4 is not square planar?*

Ans. Electronic configuration of carbon atom: C: $\sigma 1s^2\ 2s^2\ 2p^2$.

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

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



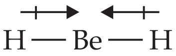
For a square planar shape, the hybridization of the central atom has to be dsp^3. However, an atom of carbon does not have *d*-orbitals to undergo dsp^3 hybridization. Hence, the structure of CH_4 is tetrahedral.

Q3. *Explain why BeH_2 molecule has a zero dipole moment although the Be–H bonds are polar.*

Ans. The Lewis structure for BeH_2 is as follows:

H **:** Be **:** H

There is no lone pair at the central atom (Be) and there are two bond pairs. Hence, BeH_2 is of the type AB_2. It has a linear structure.



Dipole moments of each H—Be bond are equal and are in opposite directions. Therefore, they nullify each other. Hence, BeH_2 has a zero dipole moment.

❑❑❑