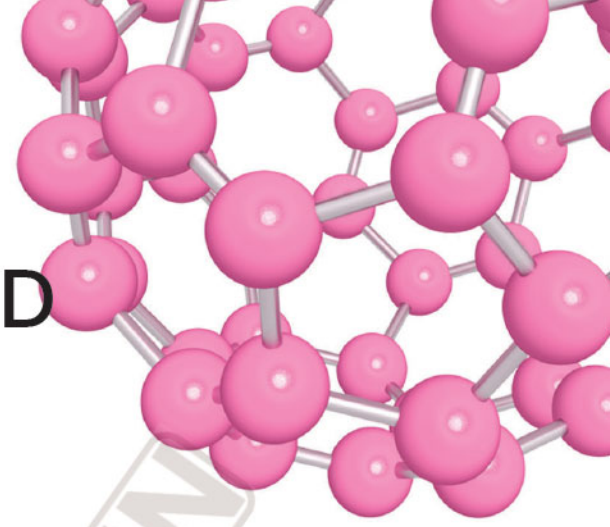
UNIT 4

CHEMICAL BONDING AND MOLECULAR STRUCTURE

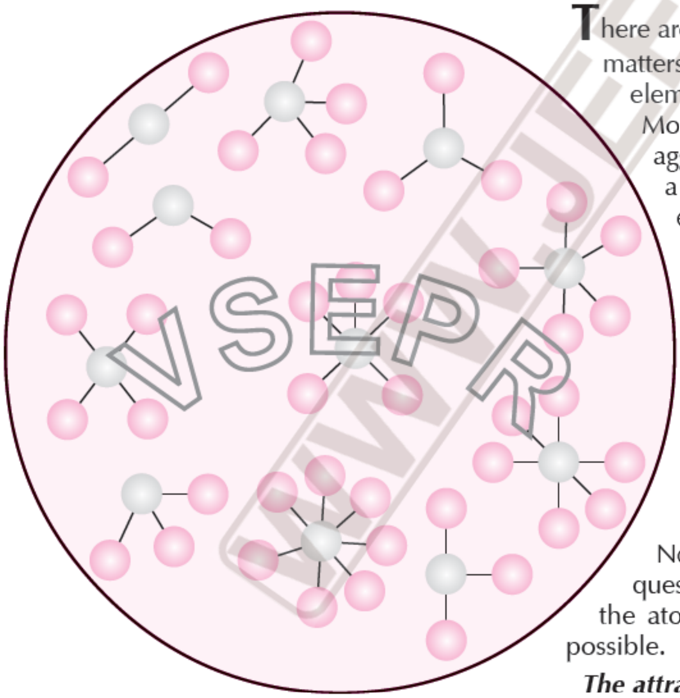


OBJECTIVES

Building on.....

Assessing.....

Preparing for Competition.....



There are about 118 different kinds of elements which constitute all matters. It is well known fact that except for noble gases, no other element exists as independent atoms under ordinary conditions. Most of these atoms exist as molecules which are cluster or aggregates of atoms or ions of same or different elements having a distinct existence and its own characteristic properties. The existence of a large number of molecules or compounds raises many questions, such as :

(*i*) Why do atoms combine?
(*ii*) Why do certain atoms combine whereas others do not?
(*iii*) What is the nature of the forces which hold the atoms together
in molecules?
(*iv*) Why do atoms have fixed combining capacity?
(*v*) Why do molecules possess definite shapes?

In Unit 2, we have studied the structure of an atom. Now, we proceed to seek answers to the above important questions, laying stress on the nature of links or bonds between the atoms and the forces which make such linkages or bonds possible.

The attractive force which holds together the constituent particles (atoms, ions or molecules) in a chemical species is known as **chemical bond.**

WHY DO ATOMS COMBINE ?

A number of attempts were made to explain the formation of chemical bonds between atoms in terms of electrons. In 1916, Kossel and Lewis succeeded independently in giving first successful explanation about the cause of combination between atoms based upon the understanding of electronic configuration of noble gases.

Table 1. Electronic configurations of noble gases.

Noble gas	Atomic number	Electronic configuration	Configuration of valence shell
Helium (He)	2	$1s^2$	$1s^2$
Neon (Ne)	10	$1s^2, 2s^2\,2p^6$	$2s^2 2p^6$
Argon (Ar)	18	$1s^2, 2s^2\,2p^6, 3s^2\,3p^6$	$3s^2 3p^6$
Krypton (Kr)	36	$1s^2, 2s^2 2p^6, 3s^2\,3p^6\,3d^{10}, 4s^2\,4p^6$	$4s^2 4p^6$
Xenon (Xe)	54	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2\,4p^6\,4d^{10}, 5s^2\,5p^6$	$5s^2 5p^6$
Radon (Rn)	86	$1s^2, 2s^2\,2p^6, 3s^2\,3p^6\,3d^{10}, 4s^2\,4p^6 4d^{10}\,4f^{14}, 5s^2\,5p^6\,5d^{10}, 6s^2 6p^6$	$6s^2\,6p^6$

(*i*) **Tendency to acquire noble gas configuration or octet rule.**

It has been observed that atoms of noble gases have little or no tendency to combine with each other or with atoms of other elements. This means that these atoms must be having stable electronic configurations. The electronic configurations of these elements are given in Table 1.

From Table 1, we find that the atoms of all noble gases (with the exception of helium) have eight electrons in their valence shell. Helium on the other hand, has two electrons in its valence shell (first energy shell) because the first energy shell ($n = 1$) cannot have more than two electrons. The electronic configuration of the valence shell for all noble gas atoms except helium can be expressed as $\boldsymbol{ns^2\ np^6}$ (for helium, $1s^2$) and this represents the stable configuration and *corresponds to maximum stability*. Due to the stable configuration, the noble gas atoms neither have any tendency to gain nor lose electrons and, therefore, **their combining capacity (or valency) is zero**.

All atoms other than noble gases have less than eight electrons in their outermost shells. In other words, the outermost shells of these atoms do not have stable configurations. Therefore, they combine with each other or with other atoms to achieve stable noble gas electronic configurations ($ns^2\ np^6$ or $1s^2$). To a large extent, the elements undergo electronic re-arrangements to attain stable noble gas configurations. Thus,

> ***the tendency or urge of atoms of various elements to attain stable configuration of eight electrons in their valence shells,*** *is the* **cause of chemical combination.**

> *The* ***principle of attaining maximum of eight electrons in the valence shell of atoms,*** *is called* **octet rule.**

However, it may be noted that for hydrogen and lithium atoms, the stable configuration means two electrons which corresponds to the nearest noble gas helium.

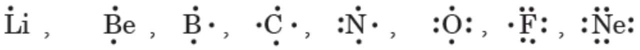
(*ii*) **Tendency to acquire minimum energy and stability.**

According to modern view, the atoms combine to form chemical bonds to acquire a state of minimum energy. As we know, every system in the universe has a natural tendency to attain a state of minimum energy. The state of minimum energy corresponds to state of maximum stability. Hence, the atoms combine with each other, *only if the process leads to lowering of energy*. If there is no fall in potential energy of the system, no bonding is possible.

LEWIS SYMBOLS

In the formation of a molecule, only the outer shell electrons take part in chemical combination. Therefore, these are also called ***valence shell electrons.*** The inner shell electrons are well protected and, therefore, they generally do not take part. G.N. Lewis, an American chemist, introduced simple notations to represent valence electrons in an atom. These notations are called *Lewis symbols* or *electron dot symbols.*

Lewis symbols or electron dot symbols According to Lewis notations, the symbol of the element represents the whole of the atom except the valence electrons (*i.e.*, nucleus and the electrons in the inner energy shells). The valence electrons are represented by placing dots (·) or crosses (×) around the symbol. For example, the Lewis symbols for the atoms of second period are :



$$\dot{\text{Li}}\ ,\quad \underset{\cdot}{\dot{\text{Be}}}\ ,\quad \underset{\cdot}{\dot{\text{B}}}\cdot\ ,\quad \cdot\underset{\cdot}{\dot{\text{C}}}\cdot\ ,\quad :\underset{\cdot}{\dot{\text{N}}}\cdot\ ,\quad :\underset{\cdot}{\dot{\text{O}}}:\ ,\quad \cdot\underset{\cdot\cdot}{\ddot{\text{F}}}:\ ,\quad :\underset{\cdot\cdot}{\ddot{\text{Ne}}}:$$

Similarly, the Lewis symbols for the elements of third period are :

$\overset{\cdot}{\text{Na}}$, $\underset{\cdot}{\overset{\cdot}{\text{Mg}}}$, $\underset{\cdot}{\overset{\cdot}{\text{Al}}}\cdot$, $\cdot\underset{\cdot}{\overset{\cdot}{\text{Si}}}\cdot$, $\cdot\underset{\cdot\cdot}{\overset{\cdot}{\text{P}}}\cdot$, $\cdot\underset{\cdot}{\overset{\cdot\cdot}{\text{S}}}:$, $\cdot\underset{\cdot\cdot}{\overset{\cdot\cdot}{\text{Cl}}}:$, $:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\text{Ar}}}:$

Significance of Lewis Symbols

(*i*) The Lewis symbols indicate the number of electrons in the outermost or valence shell.

(*ii*) These help to predict the common or **group valence** of the element. For example, lithium has one electron in valence shell and it can involve this electron in chemical combination process (by losing or sharing) and it is therefore, *monovalent;* beryllium has 2 electrons for participating in chemical combination and is *divalent.* Similarly, B and C are *trivalent* and *tetravalent* because they have three and four electrons respectively. Thus, for Li, Be, B and C, the number of electrons also indicates the common valence of these elements. However, *the common valence for N, O, F and Ne is equal to eight minus the valence electrons.* For example, for N it is 3, for O it is 2, for F it is one and for Ne it is 0. Thus,

the common valence of an element is either equal to number of dots in the Lewis symbol or it is equal to 8 minus the number of dots.

SOLVED EXAMPLES

☐ **Example 1.**

Write Lewis dot symbols for the following atoms and ions :

(i) O (ii) O^{2-} (iii) Mg^{2+} (iv) P^{3-} (v) Br

Solution: Lewis dot symbols are :

(*i*) $\cdot\underset{\cdot\cdot}{\overset{\cdot\cdot}{\text{O}}}\cdot$ (*ii*) $:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\text{O}}}:^{2-}$ (*iii*) $:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\text{Mg}}}:^{2+}$ or Mg^{2+}

(*iv*) $:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\text{P}}}:^{3-}$ (*v*) $:\underset{\cdot\cdot}{\overset{\cdot}{\text{Br}}}:$

☐ **Example 2.**

Write Lewis dot symbols for the following atoms and ions :

(i) S and S^{2-} (ii) P and P^{3-}
(iii) Al and Al^{3+} (iv) H and H^-
(v) Na ans Na^+ ***N.C.E.R.T.***

Solution: Lewis dot symbols are :

(*i*) $:\underset{\cdot}{\overset{\cdot\cdot}{\text{S}}}\cdot$ and $:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\text{S}}}:^{2-}$ (*ii*) $\cdot\underset{\cdot}{\overset{\cdot\cdot}{\text{P}}}\cdot$ and $:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\text{P}}}:^{3-}$

(*iii*) $\cdot\overset{\cdot}{\text{Al}}\cdot$ and Al^{3+} (*iv*) $\overset{\cdot}{\text{H}}$ and $\text{H}:^{-}$

(*v*) $\overset{\cdot}{\text{Na}}$ and Na^+

Practice Problems

1. Write Lewis dot symbols for atoms of the following elements :
   Mg, Na, B, O, N, Br
2. Write Lewis dot symbols for the following ions :
   Li^+, Cl^-, O^{2-}, Mg^{2+} and N^{3-}
3. Draw Lewis dot symbols for the following elements:
   (*i*) Magnesium (*ii*) Phosphorus
   (*iii*) Chlorine (*iv*) Boron
   (*v*) Xenon (*vi*) Silicon
4. Draw Lewis dot symbols for the elements of third period of the periodic table.

Answers to Practice Problems

1. $\overset{\cdot}{\text{Mg}}\cdot$, $\overset{\cdot}{\text{Na}}$, $\cdot\overset{\cdot}{\text{B}}\cdot$, $\cdot\underset{\cdot\cdot}{\overset{\cdot\cdot}{\text{O}}}\cdot$, $\cdot\underset{\cdot\cdot}{\overset{\cdot}{\text{N}}}\cdot$, $\cdot\underset{\cdot\cdot}{\overset{\cdot\cdot}{\text{Br}}}\cdot$

2. Li^+, $:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\text{Cl}}}:^{-}$, $:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\text{O}}}:^{2-}$, Mg^{2+} $:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\text{N}}}:^{3-}$

3. (*i*) $\overset{\cdot}{\text{Mg}}\cdot$ (*ii*) $\cdot\underset{\cdot}{\overset{\cdot\cdot}{\text{P}}}\cdot$ (*iii*) $:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\text{Cl}}}\cdot$

   (*iv*) $\cdot\overset{\cdot}{\text{B}}\cdot$ (*v*) $:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\text{Xe}}}:$ (*vi*) $\cdot\underset{\cdot}{\overset{\cdot}{\text{Si}}}\cdot$

OCTET RULE AND MODES OF CHEMICAL COMBINATION

In the light of octet rule, W. Kossel and G. N. Lewis, in 1916, developed an important theory of chemical combination between atoms known as *electronic theory of chemical bonding*. According to this, *atoms achieve the stable octet when they are linked by chemical bonds.* In other words, atoms combine to have an octet in their valence shells (stable noble gas configurations). They do so either by transfer of valence electrons from one atom to another (gaining or losing) or by sharing of valence electrons. Thus, *atoms combine either by transfer of valence electrons from one atom to another (gaining or losing) or by sharing of valence electrons in order to have octet in their valence shells*. This is called **octet rule**.

For example, sodium, magnesium and aluminium in the third period of the periodic table lose electrons with the formation of positive ions (cations) that have the same electronic configuration as neon ($1s^22s^22p^6$)

$$\begin{array}{cccc} \overset{\cdot}{\text{Na}} & \longrightarrow \text{Na}^+ & + & e^- \\ 1s^22s^22p^63s^1 & 1s^22s^22p^6 & & \\ \cdot\overset{\cdot}{\text{Mg}} & \longrightarrow \text{Mg}^{2+} & + & 2e^- \\ 1s^22s^22p^63s^2 & 1s^22s^22p^6 & & \\ \cdot\overset{\cdot}{\text{Al}}\cdot & \longrightarrow \text{Al}^{3+} & + & 3e^- \\ 1s^22s^22p^63s^23p^1 & 1s^22s^22p^6 & & \end{array}$$

The dots with these symbols represent electrons in the valence shell. On the other hand, oxygen and fluorine can acquire noble gas configuration by easily gaining electrons to form negative ions (anions).

$$\begin{array}{ccccc} :\underset{\cdot}{\overset{\cdot}{\text{O}}}: & + & 2e^- & \longrightarrow & :\underset{\cdot\cdot}{\overset{\cdot\cdot}{\text{O}}}:^{2-} \\ 1s^22s^22p^4 & & & & 1s^22s^22p^6 \\ :\underset{\cdot\cdot}{\overset{\cdot}{\text{F}}}: & + & e^- & \longrightarrow & :\underset{\cdot\cdot}{\overset{\cdot\cdot}{\text{F}}}:^{-} \\ 1s^22s^22p^5 & & & & 1s^22s^22p^6 \end{array}$$

In relation to chemical bonding, W. Kossel drew attention to the following facts of the periodic table :

(*i*) In the periodic table, the highly electronegative halogens are placed on the right and the highly electropositive alkali metals are present on the extreme left. These two families are separated by noble gases.

(*ii*) Halogens gain an electron to form a negative ion while alkali metals lose an electron to form a positive ion. Therefore, these ions are formed by the gain or loss of electron by their respective atoms.

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

This is *the basis of formation of chemical bonds.*

The atoms can also acquire noble gas configurations by sharing with other atoms. Therefore, there are two main types of bonds. These are :

(*i*) *Ionic bond* and

(*ii*) *Covalent bond.*

IONIC OR ELECTROVALENT BOND

When a bond is formed by the transference of one or more valence electrons of one atom to the other atom so as to complete their outermost octets and acquire stable nearest noble gas configurations, the bond formed *is called* ***electrovalent bond or ionic bond.***

In this type of bonding, one atom completes its octet and acquires noble gas configuration by losing the electrons and other by gaining the electrons. The atom which loses the electrons acquires a positive charge and the other which gains the electrons acquires a negative charge. These two oppositely charged ions, thus formed, come closer due to electrostatic forces of attraction and form an ionic bond. Thus,

the electrostatic force of attraction which holds the oppositely charged ions together is *known as* ***ionic bond or electrovalent bond.***

The compounds containing ionic or electrovalent bonds *are called* ***ionic or electrovalent compounds.***

Let us illustrate the formation of ionic bond by considering the example of sodium chloride. Sodium atom ($1s^2\ 2s^2\ 2p^6\ 3s^1$) has only one electron in the valence shell and by losing this electron, it can acquire stable electronic configuration of neon ($1s^2\ 2s^2\ 2p^6$).

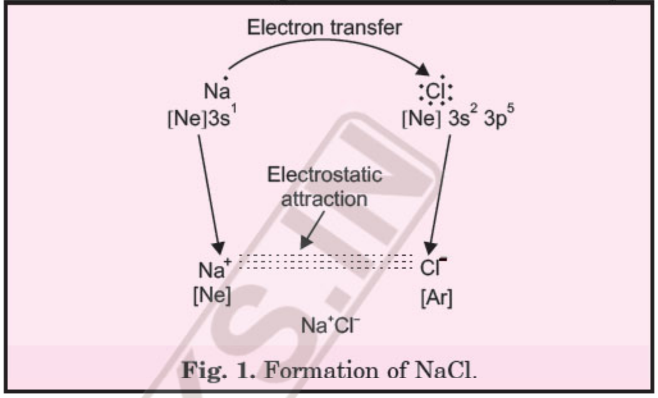
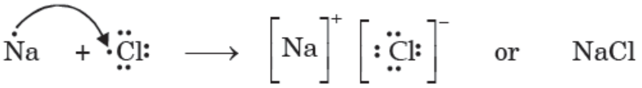


Fig. 1. Formation of NaCl.

On the other hand, chlorine atom ($1s^2\,2s^2\,2p^6\,3s^2\,3p^5$) has seven electrons in its valence shell and needs only one electron to complete its octet. Thus, both the atoms can complete their octets if sodium atom gives one electron to chlorine atom. This tendency is responsible for bonding between sodium and chlorine atoms. Therefore, sodium gives one electron and becomes positively charged Na^+ ion, while chlorine takes up the electron and becomes negatively charged, Cl^- ion. These two ions are then held together by electrostatic forces of attraction which constitute the ionic bond. In terms of Lewis structure, the ionic bond between Na and Cl may be represented as:

$$\begin{array}{ccl} \text{Na} & \longrightarrow & \text{Na}^+ \;+\; e^- \\ [\text{Ne}]\,3s^1 & & [\text{Ne}] \\ \text{Cl} + e^- & \longrightarrow & \text{Cl}^- \\ [\text{Ne}]\,3s^2 3p^5 & & [\text{Ne}]\,3s^2\,3p^6 \text{ or } [\text{Ar}] \\ \text{Na}^+ + \text{Cl}^- & \longrightarrow & \text{Na}^+\,\text{Cl}^- \text{ or NaCl} \\ & & \text{Ionic compound} \end{array}$$

Formation of sodium chloride may also be shown as :

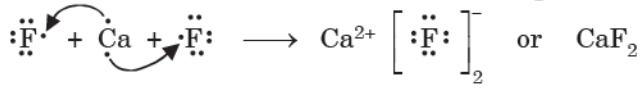


Formation of CaF_2. The electronic configurations of calcium and fluorine atoms are

Ca (Z = 20) : [Ar] $4s^2$, F (Z = 9) : [He] $2s^2 2p^5$

In the formation of calcium fluoride, calcium loses its both the valence electrons to two fluorine atoms each of which is in need of one electron. This results in the formation of Ca^{2+} ion and two F^- ions. Each of these ions acquires noble gas configuration. One Ca^{2+} and two F^- ions form bonds to give calcium fluoride. This may be represented as :

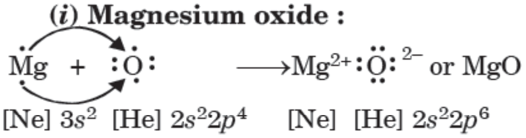
$$\begin{array}{ccl} \text{Ca} & \longrightarrow & \text{Ca}^{2+} + 2e^- \\ [\text{Ar}]\,4s^2 & & [\text{Ar}] \\ \text{F} \;+\; e^- & \longrightarrow & \text{F}^- \\ [\text{He}]\,2s^2\,2p^5 & & [\text{He}]2s^2\,2p^6 \text{ or } [\text{Ne}] \\ \text{Ca}^{2+} \;+\; 2\text{F}^- & \longrightarrow & \text{Ca}^{2+}\,2\text{F}^- \text{ or CaF}_2 \end{array}$$



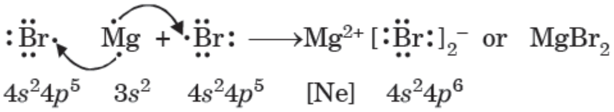
*In the formation of electrovalent bond, the number of electrons lost or gained by an atom is called its **electrovalence** or **electrovalency***. It is also equal to the number of unit charges on the ion. For example, sodium is assigned a positive electrovalence of one, calcium is assigned a positive electrovalence of two. Similarly, chlorine and fluorine both are assigned a negative electrovalence of one. Atoms that readily lose electrons are called **electropositive** while those which readily gain electrons are called **electronegative**.

Some more examples of formation of ionic bonds are:

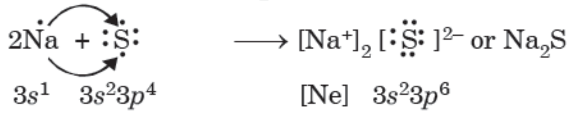
(*i*) Magnesium oxide :



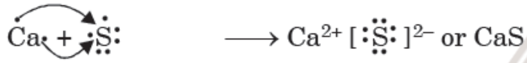
(*ii*) Magnesium bromide :



(*iii*) Sodium sulphide :



(*iv*) Calcium sulphide



FORMATION OF IONIC BOND

The formation of ionic compounds would primarily depend upon:

- The ease of formation of positive and negative ions from the respective neutral atoms.
- The arrangement of positive and negative ions in the solid. This is also called the **lattice** of the crystalline compound.

Factors on which the Formation of Ionic Bonds depend

The tendency of atoms to form ionic bonds between them depends upon the following factors :

1. Low ionization enthalpy. The ease with which an atom can lose electrons depends upon its *ionization enthalpy*. The **ionization enthalpy** is the *amount of energy required to remove the most loosely bound electron from an isolated gaseous atom to form a positive ion.*

$$M(g) \longrightarrow M^+(g) + e^- \quad \text{Ionization enthalpy}$$

Lesser the ionization enthalpy of an atom, the greater is the ease of losing the valence electron. Therefore, in general, *metals which have low ionization enthalpy values,* have greater tendency to form ionic bonds. For example, alkali and alkaline earth metals which have relatively low ionization enthalpies, generally form ionic compounds.

2. High electron gain enthalpy. The tendency of an atom to gain electrons depends upon its *electron gain enthalpy*. The **electron gain enthalpy** is the *amount of energy released when an electron is added to an isolated gaseous atom to form a negative ion.*

$$X(g) + e^- \longrightarrow X^-(g) \quad \text{Electron gain enthalpy}$$

Higher the value of negative electron gain enthalpy, greater will be the ease of formation of anion. Therefore, in general, *the elements which have high gain enthalpy values form ionic compounds***.** For example, halogen and oxygen group elements mostly form **ionic compounds**.

3. High lattice enthalpies. The formation and strength of an ionic bond also depend upon the electrostatic force of attraction between oppositely charged ions. Due to the strong electrostatic attraction between the ions, formation of the crystal results in release of energy. *The amount of energy released when free ions combine together to form one mole of a crystal* is called **lattice enthalpy** (U).

$$M^+(g) + X^-(g) \longrightarrow \underset{\substack{\text{Ionic compound} \\ \text{(1 mole)}}}{MX\,(s)} + \text{Lattice enthalpy}$$

***Higher the value of lattice enthalpy, greater will be the ease of formation of the ionic compound*.**

The ionization process is always endothermic (absorbs energy) while electron gain enthalpy process may be exothermic (releases energy) or endothermic (absorbs energy). Lattice enthalpy is exothermic (releases energy). Now, if the net effect of the above three factors is the release of energy, then ionic bond will be formed. This is in accordance with the general observation that only those processes occur in which there is decrease of energy.

Let us consider these steps for NaCl :

(*i*) $Na(g) \longrightarrow Na^+(g) + e^-$

$$\Delta_i H = 495.8 \text{ kJ mol}^{-1}$$

(*ii*) $Cl(g) + e^- \longrightarrow Cl^-(g)$

$$\Delta_{eg} H = -348.7 \text{ kJ mol}^{-1}$$

(*iii*) $Na^+(g) + Cl^-(g) \longrightarrow Na^+Cl^-(s)$

$$U = -788 \text{ kJ mol}^{-1}$$

The ionic bond is formed because the energy released in step (*ii*) and (*iii*) is more than the energy required in step (*i*). As may be calculated from the above steps, 640.9 kJ mol^{-1} of energy is released and therefore, NaCl is formed. Thus, **a quantitative measure of the stability of an ionic compound is provided by its lattice enthalpy and not simply by achieving octet of electrons around the ionic species in the gaseous state**.

Thus, to **sum up,** the conditions for stable ionic bonding are :

- **(*i*) The ionisation enthalpy of atom forming the cation should be low.**
- **(*ii*) The electron gain enthalpy of atom forming the anion should be highly negative.**
- **(*iii*) Lattice enthalpy should be high.**

LATTICE ENTHALPY OF IONIC CRYSTALS

The stability of ionic crystals is determined in terms of their lattice enthalpy. **Lattice enthalpy** is defined as

the amount of energy released when one mole of ionic crystal is formed from its constituent ions in the gaseous state.

The formation of one mole of the ionic solid from its constituent gaseous ions may be represented as :

$$M^+(g) + X^-(g) \longrightarrow MX(s); \ \Delta H = \text{Lattice enthalpy} = -U$$

The lattice enthalpy is expressed by U. The negative sign is used because energy is released in the process. Since ionic bond is formed as a consequence of electrostatic attractions between the oppositely charged ions, there is a considerable decrease of potential energy of the system. On the other hand, if one mole of solid ionic compound is broken into its constituent gaseous ions, energy will be needed which will be numerically equal to the lattice energy. Thus,

$$MX(s) \longrightarrow M^+(g) + X^-(g); \qquad \Delta H = +U$$

In this case, U has + ve sign because energy is absorbed in the process. Thus,

Lattice enthalpy may also be defined as: ***the energy required to completely separate one mole of a solid ionic compound into gaseous ionic constituents.***

It is obvious that if the compound is stable, a large amount of energy will be needed (numerically equal to lattice enthalpy). This means that *the higher the lattice enthalpy of an ionic compound, greater will be its stability.* The magnitude of lattice enthalpy gives an idea about the interionic forces. It depends upon the following factors :

(*i*) **Size of the ions.** Smaller the size of the ions, lesser is the internuclear distance. Consequently, the interionic attractions will be high and the lattice enthalpy will also be large. For example, ionic radius of K^+ (133 pm) is larger than that of Na^+ (95 pm), therefore, the lattice enthalpy of NaCl (758.7 kJ mol^{-1}) is greater than that of KCl (681.4 kJ mol^{-1}).

(*ii*) **Charge on the ions.** Larger the magnitude of charge on the ions, greater will be the attractive forces between the ions. Consequently, the lattice enthalpy will be high.

Lattice enthlpies of some ionic compounds are given in Table 2.

It is evident from the Table 2 that the lattice enthalpies of ionic solids are quite high. This is because of the strong electrostatic attractions between oppositely charged ions present in the solid. Since coulombic forces of attraction vary directly as the product of the charges, it follows that the higher the valency (charge) of the ions, the greater would be the lattice enthalpy of the ionic solid. Thus, lattice enthalpy increases as we move from uni-univalent ionic solids to uni-bivalent ionic solids and then to bi-bivalent ionic solids.

It may be noted that most of the ionic compounds have cations derived from metallic elements and anions from non-metallic elements. The ammonium ion, NH_4^+ (made up of two non-metallic elements) is an exception. It forms the cation of a number of ionic compounds.

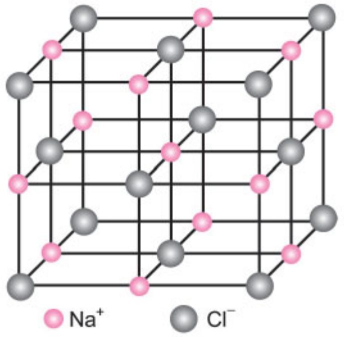
Table 2. Lattice enthalpies of some ionic solids.

Uni-univalent solids		Bi-univalent solids		Bi-bivalent solids	
Ionic solid	**Lattice enthalpy (kJ mol^{-1})**	**Ionic solid**	**Lattice enthalpy (kJ mol^{-1})**	**Ionic solid**	**Lattice enthalpy (kJ mol^{-1})**
LiF	–1033	CaF_2	–2581	BeO	–3125
CsF	–748	$CaCl_2$	–2254	MgO	–3932
NaCl	–758	MgF_2	–2882	MgS	–3254
NaBr	–752	$MnCl_2$	–2525	ZnO	–4032
LiI	–140				
CsI	–601				
AgCl	–895				
AgI	–795				

GENERAL PROPERTIES OF IONIC COMPOUNDS

The general properties of ionic compounds are :

1. Physical state. Ionic compounds usually exist in the form of crystalline solids. X-rays studies of these compounds show that these compounds do not exist as independent molecules but exist in the form of ions. These ions are arranged in some definite geometric patterns to form the crystal lattice. For example, in NaCl crystal, each Na^+ ion is surrounded by six Cl^- ions and each Cl^- ion is surrounded by six Na^+ ions. ***The number of oppositely charged ions present as the nearest neighbours around an ion* is called its coordination number.** Thus, coordination number of Na^+ in NaCl ionic crystal is 6 and similarly, the coordination number of Cl^- ion in NaCl crystal is 6. The crystal structure of sodium chloride (called rock salt) is shown.



The geometric arrangement of different substances is different. It depends upon the size of the ions and the magnitude of the charges on the ions.

2. Melting and boiling points. Ionic compounds have high melting and boiling points. This is because the ions are held together by strong electrostatic forces of attractions and hence large amount of energy is required to break the crystal lattice. The variation in melting point depends upon the charges on the ions and ionic radii. The closer the ions in crystal, the larger will be the electrostatic forces of attraction and consequently, higher will be the melting point. For example, in case of sodium halides the melting points decrease from NaF to NaI : NaF (1270 K), NaCl (1073 K), NaBr (1023 K) and NaI (924 K).

3. Solubility. Ionic compounds are generally soluble in water and other polar solvents having high dielectric constants. This is due to larger electrostatic interactions between polar solvents and ions. However ionic compounds are insoluble in non-polar solvents.

4. Electrical conductivity. Ionic compounds are good conductors of electricity in the solution or in their molten states. In the solution or in their molten states, the ions become free to move. However, these do not conduct in their solid state because of strong electrostatic forces between the ions.

5. Ionic reactions. The ionic compounds split up into oppositely charged ions when dissolved in water. The chemical reactions of ionic compounds are characteristic of the constituent ions and are known as **ionic reactions**. Such reactions occur almost instantaneously.

6. Non-directional character. The ionic bond is non-directional. In ionic-compounds, each ion is surrounded by oppositely charged ions uniformly distributed all around the ion and therefore, electrical field is non-directional. Thus, the ionic bond is non-directional.

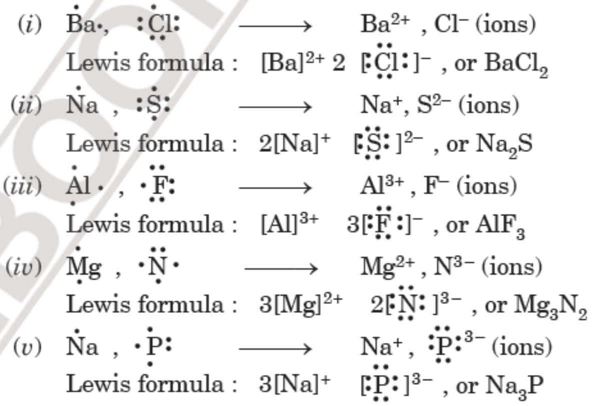
SOLVED EXAMPLES

☐ **Example 3.**

Give the Lewis structures and empirical formulae for the ionic compounds formed between the following pairs of elements :

(i) Ba, Cl (ii) Na, S (iii) Al, F (iv) Mg, N (v) Na, P

Solution: From the charges on the ions, the number of positive and negative ions in the compound can be found out. This gives the empirical formula (E.F.)



(*i*) $\dot{\text{Ba}}\cdot,\ :\dot{\underset{\cdot\cdot}{\text{Cl}}}: \longrightarrow Ba^{2+}, Cl^-$ (ions)

Lewis formula : $[Ba]^{2+}\ 2\,[:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{Cl}}}:]^-$, or $BaCl_2$

(*ii*) $\dot{\text{Na}},\ :\dot{\underset{\cdot}{\text{S}}}: \longrightarrow Na^+, S^{2-}$ (ions)

Lewis formula : $2[Na]^+\ [:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{S}}}:]^{2-}$, or Na_2S

(*iii*) $\dot{\underset{\cdot}{\text{Al}}}\cdot,\ \cdot\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{F}}}: \longrightarrow Al^{3+}, F^-$ (ions)

Lewis formula : $[Al]^{3+}\ 3[:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{F}}}:]^-$, or AlF_3

(*iv*) $\dot{\underset{\cdot}{\text{Mg}}},\ \cdot\overset{\cdot\cdot}{\underset{\cdot}{\text{N}}}\cdot \longrightarrow Mg^{2+}, N^{3-}$ (ions)

Lewis formula : $3[Mg]^{2+}\ 2[:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{N}}}:]^{3-}$, or Mg_3N_2

(*v*) $\dot{\text{Na}},\ \cdot\dot{\underset{\cdot}{\text{P}}}: \longrightarrow Na^+, :\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{P}}}:^{3-}$ (ions)

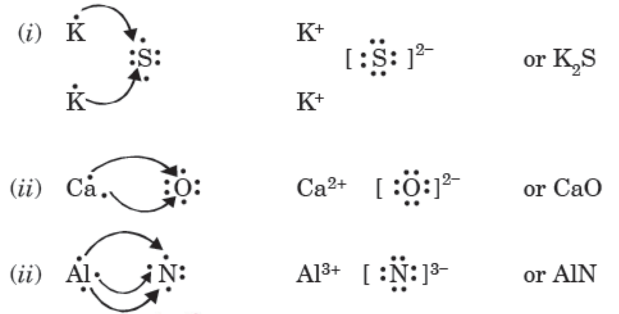
Lewis formula : $3[Na]^+\ [:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{P}}}:]^{3-}$, or Na_3P

☐ **Example 4.**

Use Lewis symbols to show electron transfer between the following atoms to form cations and anions : ***N.C.E.R.T.***

(*i*) *K* and *S* (*ii*) *Ca* and *O* (*iii*) *Al* and *N*

Solution:



Practice Problems

5. Draw the Lewis structures for the following ionic compounds :

(*i*) Li_2O (*ii*) $CaCl_2$ (*iii*) LiF

6. Draw the Lewis structures for K_2O and $MgCl_2$.

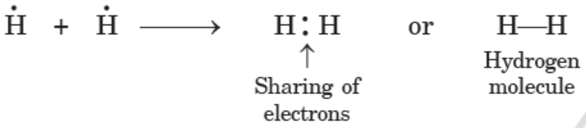
COVALENT BOND

In 1919, Langmuir refined the Lewis postulations and introduced the term **covalent bond.** According to Lewis–Langmuir theory, atoms can combine by sharing of electrons between them. This type of bond is called covalent bond and each atom contributes equal number of electrons for sharing in order to acquire configuration of nearest noble gas. Thus,

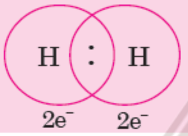
the bond formed by mutual sharing of electrons between the combining atoms of the same or different elements is called a **covalent bond.**

The compounds so formed are called **covalent compounds.**

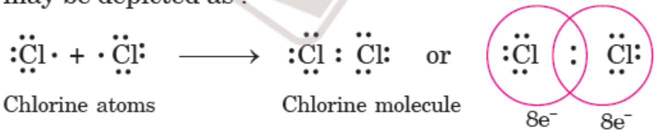
Let us consider the formation of a hydrogen molecule from two hydrogen atoms. When two hydrogen atoms approach each other, the single electron of both the atoms forms a shared pair. The shared pair now belongs simultaneously to both the hydrogen atoms *i.e., it is contained by electron shells of both the atoms.* Each hydrogen atom can now be thought of as having noble gas configuration of helium ($1s^2$). This may be represented as :



The sharing of electrons can also be shown by drawing a circle around each atom. This also helps us to count the electrons around any atom; the shared electron pair is thought of as belonging exclusively to that atom. For example, H_2 molecule is shown as



Similarly, two chlorine atoms combine with each other to form a molecule of chlorine. In this case, both the atoms have seven electrons in the outermost shell ([Ne] $3s^2\ 3p^5$) and have one electron less than argon configuration. Therefore, they contribute one electron each to form a shared pair between two atoms. In this process, both chlorine atoms attain the stable electronic configuration of noble gas (octet). This results in the formation of a covalent bond in Cl_2 molecule. This may be depicted as :



Chlorine atoms

Chlorine molecule

However, a covalent bond is not only formed between similar atoms but it may also be formed between dissimilar atoms. For example, hydrogen and chlorine form a covalent bond between their atoms. In HCl, hydrogen atoms has only one electron and chlorine atom has seven electrons in its valence shell. Therefore, by mutual sharing of electron pair between a hydrogen atom and a chlorine atom, both the atoms acquire nearest noble gas configurations. Hydrogen atom acquires electronic configuration of helium whereas chlorine atom gets electronic configuration of argon.

Hydrogen chloride

Lewis Structures and Covalent Bond

Conditions for writing the Lewis dot structures of molecules

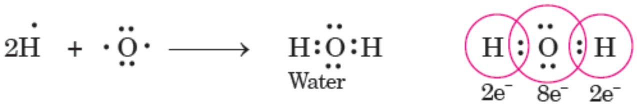
The main conditions for writing the electron dot (or Lewis) structures of covalent molecules are :

(*i*) Each bond is formed as a result of sharing of an electron pair between the atoms.

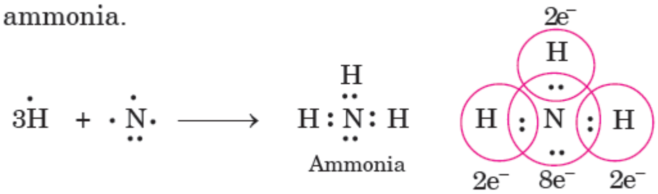
(*ii*) Each combining atom contributes one electron to the shared pair.

(*iii*) Both the combining atoms attain the stable outer shell noble gas configurations as a result of sharing of the electrons. In other words, octets of both the atoms get completed.

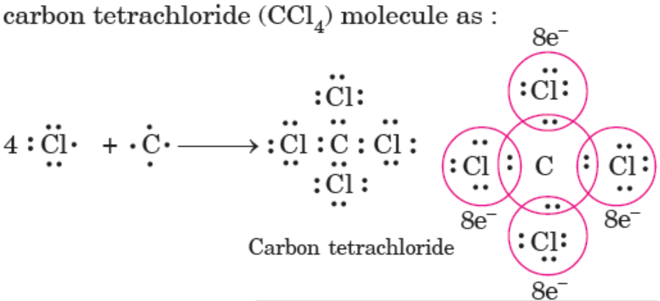
Electron dot (or Lewis) structures of covalent molecules are written in accordance with octet rule. According to this, all the atoms in a formula will have a total of eight electrons in the valence shell (shown) except the hydrogen atom. Hydrogen will have only two electrons because only two electrons complete its first shell as in helium. Thus, the elements of group 17 (containing seven valence electrons) such as Cl, would share one electron to attain stable octet; the elements of group 16 (containing six valence electrons) such as O and S would share two electrons; the elements of group 15 (containing five valence electrons) would share three electrons and so on. For example, oxygen (with six electrons in the valence shell) completes its octet by sharing its two electrons with two hydrogen atoms as shown below :



Similarly, nitrogen has five electrons in its valence shell and shares with three hydrogen atoms to form ammonia.



Similarly, carbon has four electrons in its valence shell and shares with four chlorine atoms to form carbon tetrachloride (CCl_4) molecule as :



Lewis structures for molecules having multiple covalent bonds. If the normal valence of an atom is not satisfied by sharing single electron pair between atoms, the atoms may share more than one electron pair between them.

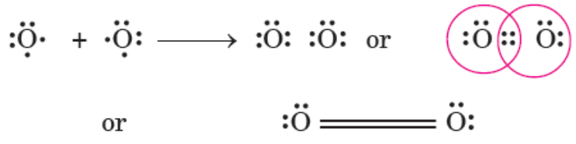
(*i*) *If two atoms share one electron pair*, bond is known as **single covalent bond** and is represented by one dash (—).

(*ii*) *If two atoms share two electron pairs*, bond is known as **double covalent bond** and is represented by two dashes (═).

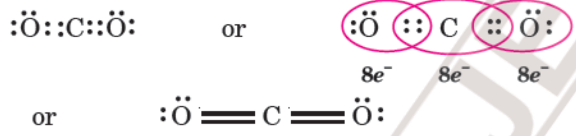
(*iii*) *If two atoms share three electron pairs*, bond is known as **triple covalent bond** and is represented by three dashes (≡).

Let us discuss some examples of molecules having double and triple bonds.

Oxygen molecule. In the formation of oxygen molecule, each oxygen atom has six electrons in the valence shell and requires two electrons to complete its octet. Therefore, both the atoms contribute two electrons each for sharing to form oxygen molecule. In this molecule, two electron pairs are shared and hence there is a double bond between the two oxygen atoms.

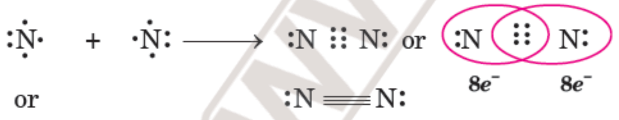


Carbon dioxide molecule. Carbon has four valence electrons and oxygen has six. To complete the octets, carbon shares two of its valence electrons with one oxygen atom and two with other oxygen atom.

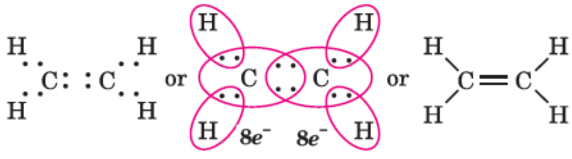


Thus, there are two double bonds in CO_2 molecule.

Nitrogen molecule. In the formation of a nitrogen molecule, each of the two nitrogen atoms having five valence electrons, provides three electrons to form three electron pairs for sharing. Thus, a triple bond is formed between the two nitrogen atoms.

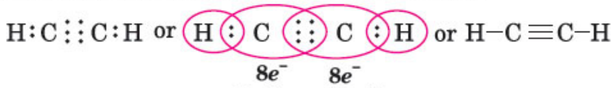


Ethylene molecule. In ethylene, each carbon atom shares two of its valence electrons with two hydrogen atoms and remaining two electrons with the second carbon atom. So, there is a double bond between carbon atoms.



C_2H_4 molecule

Acetylene molecule. In acetylene molecule, each carbon atom shares three of its valence electrons with other carbon atom forming a triple bond.



C_2H_2 molecule

Writing Lewis structures

The following steps are adopted for writing the Lewis dot structures or Lewis structures :

Step 1. Calculate the total number of electrons required for writing the structure by adding the valence electrons of the combining atoms. For example, in methane, CH_4 molecule, there are 8 valence electrons (4 from carbon and 4 from four H atoms).

Step 2. For anions, each negative charge means addition of an electron to the valence electrons and for cations, each positive charge means subtraction of one electron from the valence electrons.

Step 3. Knowing the chemical symbols of the combining atoms and guessing the skeletal structure of the compound, distribute the total number of electrons as bonding shared pairs between the atoms in proportion to the total bonds.

Step 4. In general, the least electronegative atom occupies the central position in the molecule. Hydrogen and fluorine generally occupy the terminal positions.

Step 5. After distributing the shared pairs of electrons for single bonds, the remaining electron pairs are used either for multiple bonds or they constitute lone pairs.

The basic requirement is that each bonded atom gets an octet of electrons.

Let us learn these steps by writing Lewis structures for some molecules or ions.

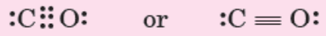
(*i*) **Lewis formula for carbon monoxide, CO**

Step 1. Counting the total number of valence electrons of carbon and oxygen atoms :
C ($2s^22p^2$) + O ($2s^22p^4$)
4 + 6 = 10. *i.e.*, 4(C) + 6(O) =10

Step 2. The skeletal structure of CO is written as:
CO

Step 3. Drawing of a single bond between C and O and completing octet on O, the remaining two electrons are the lone pair on C.

Step 4. This does not complete octet on carbon and, hence, we have triple bond between C and O atom.



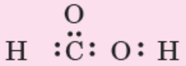
This satisfies octet rule condition for both atoms.

(*ii*) **Lewis formula for formic acid (HCOOH)**

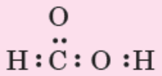
Step 1. Counting the total number of valence electrons
Total number of valence electrons are:
C ($2s^22p^2$) + 2H($1s^1$) + 2O ($2s^22p^4$)
4 + 2 × 1 + 2 × 6 = 18.

Step 2. The skeletal structure of formic acid suggested by molecular formula is :

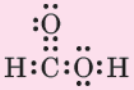
HCOOH or



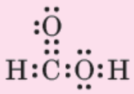
Step 3. Use four electron pairs to form single bond between neighbouring atoms



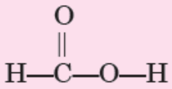
Step 4. Complete octet of each atom (except H) by adding two lone pairs on each oxygen atom and one oxygen gets double bond between C and O.



Hence the final Lewis structure is



or



(*iii*) Lewis structure of nitrite, NO_2^- ion

Step 1. Counting the total number of valence electrons of one nitrogen atom, two oxygen atoms and the additional one negative charge (equal to one electron).

Total number of valence electrons are :

$N(2s^22p^3) + 2O(2s^22p^4) + 1$ (–ve charge)

$5 + 2 \times 6 + 1 = 18$

Step 2. The skeletal structure of NO_2^- ion is written as :

O N O

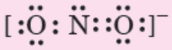
Step 3. Draw single bonds between nitrogen and each oxygen atom.

O : N : O

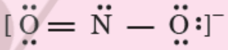
Step 4. Complete the octets of atoms.

This structure does not complete octet on N if the remaining two electrons constitute a lone pair on it . Therefore, we have double bond between one N and one of the two O atoms.

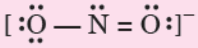
or



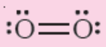
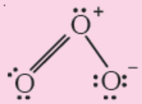
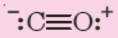
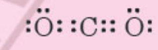
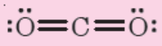
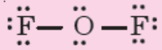
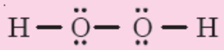
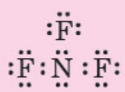
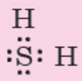
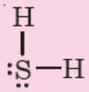
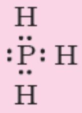
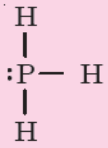
The Lewis structure is

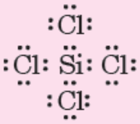
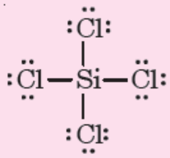
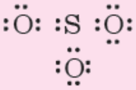
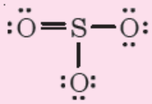
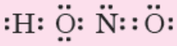
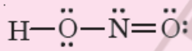
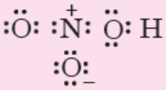
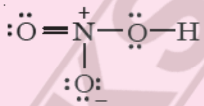
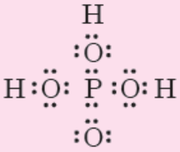
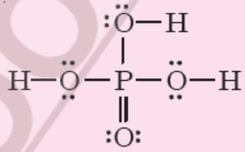
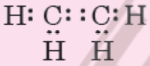
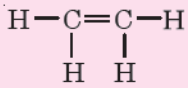
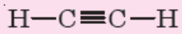
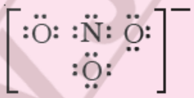
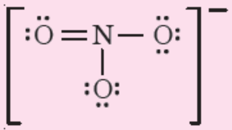
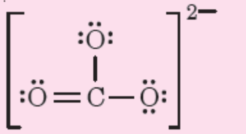
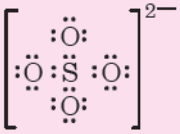
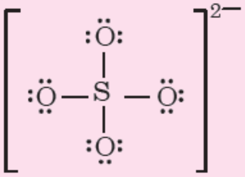
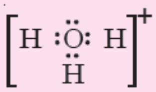
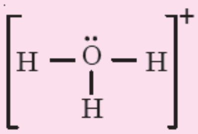
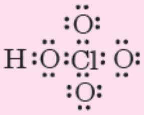
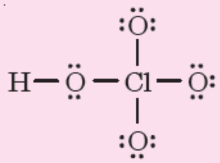


or



Lewis dot representation of some molecules or ions are summarized below :

Molecule/ion	**Lewis Representation**		
O_2		or	
O_3		or	
CO		or	
CO_2		or	
OF_2		or	
H_2O_2		or	
NF_3		or	
H_2S		or	
PH_3		or	

$SiCl_4$		or	
SO_3		or	
HNO_2 (Nitrous acid)		or	
HNO_3 (Nitric acid)		or	
H_3PO_4 (Phosphoric acid)		or	
C_2H_4 (Ethylene)		or	
C_2H_2 (Acetylene)		or	
NO_3^-		or	
CO_3^{2-}		or	
SO_4^{2-}		or	
H_3O^+		or	
$HClO_4$ (Perchloric acid)		or	

Formal charge

In case of polyatomic ions, the net charge is possessed by the ion as a whole and not by a particular atom. It is possible, however, to assign a formal charge on each atom. The ***formal charge of an atom in a polyatomic ion or molecule*** is defined as

> ***the difference between the number of valence electrons in an isolated (or free) atom and the number of electrons assigned to that atom in a Lewis structure.***

It may be expressed as :

Formal charge on an atom in a Lewis structure =

$$\begin{pmatrix}\text{total number of}\\ \text{valence electrons}\\ \text{in free atom}\end{pmatrix} - \begin{pmatrix}\text{total number of}\\ \text{nonbonding}\\ \text{(lone pair) electrons}\end{pmatrix} - \frac{1}{2}\begin{pmatrix}\text{total number of}\\ \text{bonding}\\ \text{(shared) electrons}\end{pmatrix}$$

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

where FC = Formal charge on an atom

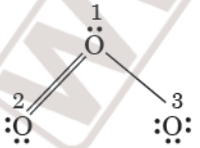
V = Total number of valence electrons in the free atom

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

S = Total number of bonding (shared) electrons.

The counting is based on the assumption that each atom owns one electron of each bonding pair and both the electrons of a lone pair. We can count the number of electrons assigned to an atom on this assumption and then compare the number with the number of electrons in the free atom. If the atom has more electrons in the molecule than in the free or neutral atom, then the atom has a negative formal charge. On the other hand, if the atom has less electrons in the molecule than in the free or neutral atom, then it has a positive formal charge.

Let us consider ozone molecule. The ozone molecule may be represented as :



The central O atom marked 1 has 6 valence electrons, one lone pair (2 electrons) and three bonds (or 6 bonding electrons). Therefore, its formal charge is

$$\text{FC on O (1)} = 6 - 2 - \frac{1}{2} \times 6 = +1$$

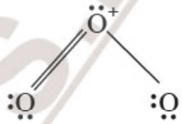
The end O atom marked 2 has 6 valence electrons, two lone pairs (4 electrons) and two bonds (4 bonding electrons). Therefore, its formal charge is

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

The end O atom marked 3 has 6 valence electrons, three lone pairs (6 electrons) and one bond (2 bonding electrons). Therefore, its formal charge is

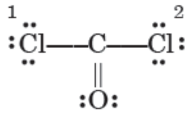
$$\text{FC on O (3)} = 6 - 6 - \frac{1}{2}(2) = -1$$

Therefore, the formal charges on the oxygen atoms in the Lewis structures of ozone molecule are written as :



It may be noted that formal charges do not indicate real charge separation within the molecules. *These only help in keeping track of the valence electrons in the molecule.* **The formal charges help in the selection of the lowest energy structure from a number of possible Lewis structures for a given molecule or ion. In general, the lowest energy structure is the one, which has lowest formal charges on the atoms.**

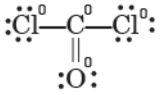
Let us consider another example of phosgene ($COCl_2$) which is a poisonous gas.



Cl (1)	**Cl (2)**
Valence electrons = 7	Valence electrons = 7
Lone pair electrons = 6	Lone pair electrons = 6
Bond pair electrons = 2	Bond pair electrons = 2
$\therefore FC = 7 - 6 - \frac{1}{2}(2)$	$\therefore FC = 7 - 6 - \frac{1}{2}(2)$
$= 0$	$= 0$

O atom	**C atom**
Valence electrons = 6	Valence electrons = 4
Lone pair electrons = 4	Lone pair electrons = 0
Bond pair electrons = 4	Bond pair electrons = 8
$\therefore FC = 6 - 4 - \frac{1}{2}(4)$	$\therefore FC = 4 - 0 - \frac{1}{2}(8)$
$= 0$	$= 0$

Thus,



Exceptions to the Octet Rule.

Although octet rule is useful in a large number of cases, it has many exceptions also. Some important exceptions of octet rule are given below :

1. Hydrogen molecule. Hydrogen has one electron in its first energy shell ($n = 1$). It needs only one more electron to fill this shell, because the first shell cannot have more than two electrons. This configuration ($1s^2$) is similar to that of noble gas helium and is stable. In this case, therefore, octet is not needed to achieve a stable configuration.

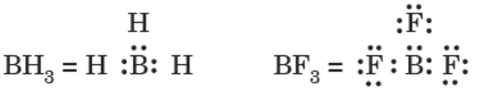
2. Incomplete octet of the central atom. The octet rule cannot explain the formation of certain molecules of lithium, beryllium, boron, aluminium, etc. (LiCl, BeH_2, $BeCl_2$, BH_3, BF_3) in which the central atom has less than eight electrons in the valence shell. These are electron deficient compounds as shown below :

LiCl = Li :Cl:

2 electrons around central Li-atom

BeH_2 = H : Be : H $BeCl_2$ = :Cl: Be :Cl:

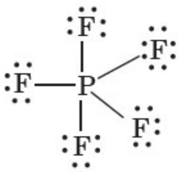
4 electrons around central Be-atom



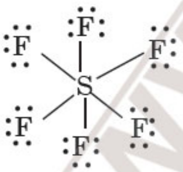
BH_3 = H :B: H BF_3 = :F : B: F:

6 electrons around central B-atom

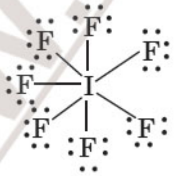
3. Expanded octet of the central atom. There are many stable molecules which have more than eight electrons in their valence shells. For example, PF_5 has ten; SF_6 has twelve and IF_7 has fourteen electrons around the central atoms, P, S and I respectively, as shown below :



(10 electrons around P)

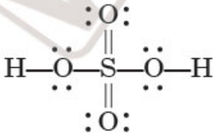


(12 electrons around S)



(14 electrons around I)

Similarly, in sulphuric acid, there are twelve electrons around the sulphur atoms.



12 electrons around S atom

These compounds in which the atom has more than 8 electrons around it are called **hypervalent compounds.**

However, it may be noted that sulphur also forms many compounds in which the octet rule is obeyed. For example, in sulphur dichloride, the S atom has an octet of electrons around it.

:Cl:S:Cl: or   :Cl—S—Cl:

4. Odd electron molecules. There are certain molecules which have odd number of electrons, like nitric oxide, NO and nitrogen dioxide, NO_2. In these cases, octet rule is not satisfied for all the atoms.

Nitric oxide   Nitrogen dioxide

The other examples of molecules having odd number of electrons are ozone (O_3), superoxide ion (O_2^-) etc.

Other drawbacks of the octet rule

5. It may be noted that the octet rule is based upon the chemical inertness of noble gases. However, it has been found that some noble gases (especially xenon and krypton) also combine with oxygen and fluorine to form a large number of compounds such as XeF_2, KrF_2, $XeOF_2$, $XeOF_4$, XeF_6, etc.

6. This theory does not account for the shape of the molecules.

7. It cannot explain the relative stability of the molecule in terms of the energy.

GENERAL PROPERTIES OF COVALENT COMPOUNDS

The main characteristic properties of covalent compounds are :

1. State of existence. The covalent compounds do not exist as ions but they exist as molecules. There are weak intermolecular forces between the molecules and hence, they exist as liquids or gases at room temperature. However, a few compounds also exist in the solid state *e.g.*, urea, sugar, etc.

2. Low melting and boiling points. The melting and boiling points of covalent compounds are generally low. This is because of the fact that the forces between the molecules are weak and are easily overcome at low temperatures.

3. Solubility. Covalent compounds are generally insoluble or less soluble in water and other polar solvents. However, these are soluble in non-polar solvents such as benzene, carbon-tetrachloride, etc.

4. Non-conductors. Since covalent compounds do not give ions in solution, these are poor conductors of electricity in the fused or dissolved state.

5. Molecular reactions. The reactions between covalent compounds occur between their molecules. These involve the breaking of covalent bonds in reacting molecules and forming new covalent bonds to give molecules of the products. These **reactions are quite slow** because energy is required to break covalent bonds.

6. Directional character of bond. Since the covalent bond is localised in between the nuclei of atoms, it is directional in nature.

SOLVED EXAMPLES

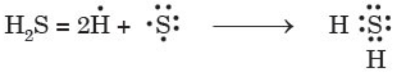
☐ **Example 5.**

Draw Lewis structures for the following molecules and identify the atoms in each of the following which do not obey octet rule :

H_2S SF_2 BF_3 SO_2 PCl_3

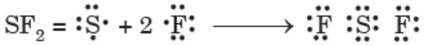
Solution: The Lewis structures for the molecules may be written on the basis of number of electrons in the valence shell of the central atom, and shared electron pairs with the other atoms as shown below :

(*i*)



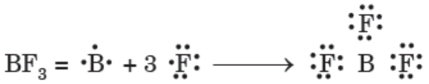
Two H-atoms do not obey octet rule.

(*ii*)



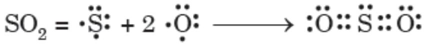
All atoms obey octet rule.

(*iii*)



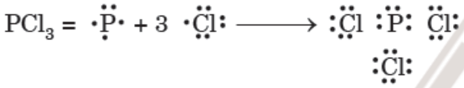
Boron does not obey octet rule.

(*iv*)



S-atom does not obey octet rule.

(*v*)



All atoms obey octet rule.

☐ **Example 6.**

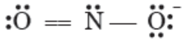
Calculate the formal charges on the atoms in

(i) Nitrite ion

(ii) Carbonate ion

Solution:

(*i*) Lewis structure of nitrite ion is



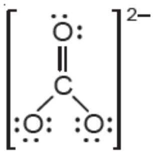
$$\text{FC on N atom} = V - L - \frac{1}{2}S$$

$$= 5 - 2 - \frac{1}{2}(6) = 0$$

$$\text{FC on double bonded O atom} = 6 - 4 - \frac{1}{2}(4) = 0$$

$$\text{FC on single bonded O atom} = 6 - 6 - \frac{1}{2}(2) = -1$$

(*ii*) Lewis structure of carbonate ion is



$$\text{FC on C atom} = 4 - 0 - \frac{1}{2}(8) = 0$$

FC on double bonded O atom

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

FC on single bonded O atom

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

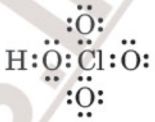
☐ **Example 7.**

Calculate the formal charge on

(i) Cl in $HClO_4$ (ii) S in HSO_4^-

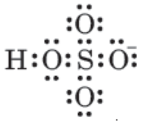
Solution:

(*i*) Lewis structure of $HClO_4$ is



$$\text{FC on Cl atom} = 7 - 0 - \frac{1}{2}(8) = +3$$

(*ii*) Lewis structure of HSO_4^- is



$$\text{F.C. on S atom} = 6 - 0 - \frac{1}{2}(8)$$

$$= 6 - 4 = +2$$

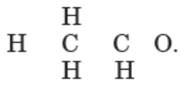
Practice Problems

7. Draw Lewis dot structures for the following molecules :

(*a*) CCl_4 (*b*) F_2O (*c*) PF_3 (*d*) F_2

(*e*) ClF_3 (*f*) NCl_3 (*g*) HONO

8. The skeleton structure for acetaldehyde (CH_3CHO) is :



Draw its Lewis structure.

9. Draw Lewis structures for the following molecules and ions :

AlI_3, $SiCl_4$, CO_3^{2-}, HCOOH

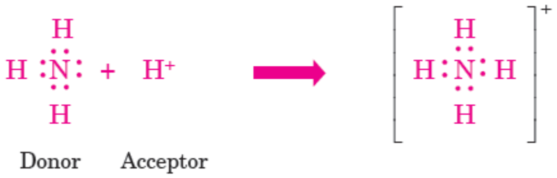
10. Write the Lewis structures for

(*i*) CO (*ii*) NH_2CONH_2 (urea)

(*iii*) H_2CCH_2 (ethene) (*iv*) HNO_3

CO-ORDINATE COVALENT BOND

So far, we have considered that in single covalent bonds each atom contributes one electron. The shared pair of electrons is provided to a bond by one atom only and the other atom merely participates in sharing. Perkin (in 1921), suggested another covalent type bond in which *both the electrons in the shared pair come from one atom. This is called* a **coordinate covalent bond.** Such type of bond is formed between atoms (or ions), one of which is deficient in at least two electrons while the other atom has already acquired a stable noble gas configuration (or octet). The atom which contributes the electrons is called the **donor** while the other which only shares the electron pair is known as **acceptor.** *This bond is usually represented by an arrow (⟶) pointing from donor to the acceptor atom.* This type of bond has also been named as **dative bond, donor-acceptor bond, semi-polar bond or co-ionic bond.** For example, a hydrogen ion combines with ammonia molecule by a coordinate covalent bond to form ammonium ion (NH_4^+):

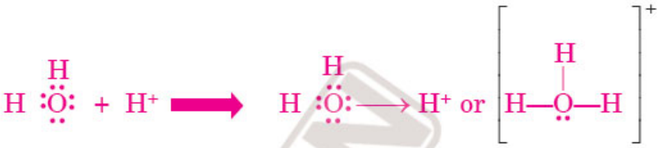


> *It may be remembered that in the modern terminology, there is no distinction between a covalent bond and a coordinate bond. Once the coordinate bond is formed, it cannot be distinguished from the normal covalent bond.*

A few examples of this type of bond are given below :

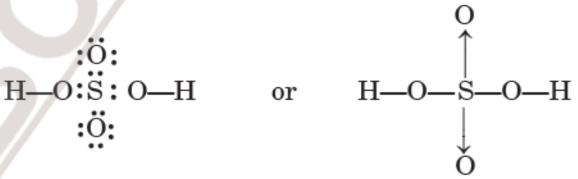
(i) **Ozone molecule (O_3).** A molecule of oxygen contains two oxygen atoms joined by double covalent bond so that octet of each of the two atoms is complete. Now, if an atom of oxygen having six electrons comes close to oxygen molecule, the new atom may share a lone pair of electrons of one of the oxygen atoms of the oxygen molecule. This results in the formation of a co-ordinate bond as shown below :

(ii) **Hydronium ion (H_3O^+).** Water, (H_2O) has two lone pairs of electrons on oxygen atom while H^+ ion has empty 1*s*-shell. Thus, oxygen atom can easily donate two electrons to H^+ ion.



(iii) **Ammonia (NH_3) and boron trifluoride (BF_3).** These molecules also combine through a co-ordinate bond as shown below :

(iv) **Sulphuric acid, (H_2SO_4).** Sulphuric acid has also two co-ordinate bonds in its molecule. As given below, the bonds between the sulphur atom and the oxygen atom of two — OH groups are the normal single bonds, whereas, the bonds between sulphur atom and the other two oxygen atoms are co-ordinate bonds.



add on Conceptual Questions 1

Q. 1. Out of MgO and NaCl, which has higher lattice energy and why ?

Ans. MgO has higher lattice energy because both the ions carry two unit charges whereas in NaCl, each ion carries one unit charge.

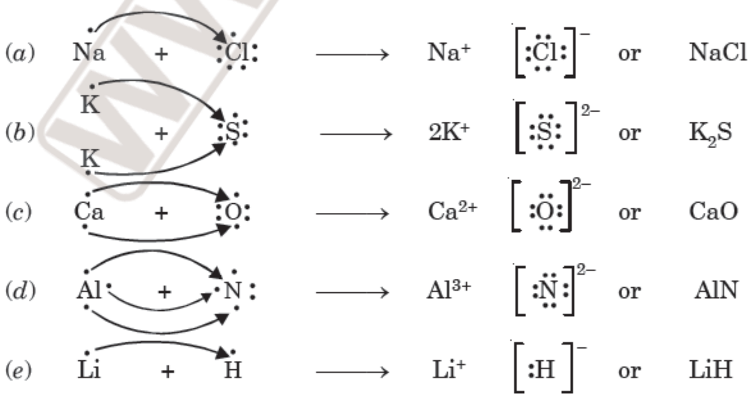
Q. 2. Why is NaCl a bad conductor of electricity in the solid state ?

Ans. In the solid state, Na^+ and Cl^- ions are strongly held together and are not free to move.

Q. 3. Use Lewis dot symbols to show electron transfer between the following atoms to form cations and anions :

(a) Na and Cl (b) K and S (c) Ca and O (d) Al and N (e) Li and H

Ans.



Q. 4. Write Lewis dot symbols for the following elements :
Mg, Na, B, O, N, Br

N.C.E.R.T.

Ans.

CONCEPTUAL QA

Q. 5. Write Lewis symbol for the following stoms and ions :
S and S^{2-}, Al and Al^{3+}, H and H^- N.C.E.R.T.

Ans. $:\underset{\cdot}{\ddot{S}}\cdot$ and $:\underset{\cdot\cdot}{\ddot{S}}:^{2-}$ $\cdot\dot{Al}\cdot$ and Al^{3+} $\dot{H}$ and $\ddot{H}^{-}$

Q. 6. Write Lewis dot symbols for O and O^{2-}

Ans. $\cdot\underset{\cdot}{\ddot{O}}:$ and $:\underset{\cdot\cdot}{\ddot{O}}:^{2-}$

Q. 7. Which of the two is more hard : MgO or CaO ? The internuclear distances of MgO and CaO are 2.05 and 2.40 Å respectively.

Ans. MgO because MgO has less interionic distance than CaO (both have same charges) and, therefore, electrostatic force of attraction is more in MgO.

Q. 8. Why does NaCl give a white precipitate with $AgNO_3$ solution but CCl_4 does not ?

Ans. NaCl is an ionic compound and gives Cl^- ions in the solution. These Cl^- ions react with Ag^+ ions given by $AgNO_3$ to form a white precipitate of AgCl.

$$Cl^- \text{ (from NaCl)} + Ag^+ \text{ (from } AgNO_3) \longrightarrow \underset{\text{White ppt.}}{AgCl}$$

However, CCl_4 is a covalent compound and does not give Cl^- ions to react with Ag^+ (or $AgNO_3$).

Q. 9. Calculate the formal charge on each atom in

$$:\underset{\cdot\cdot}{\ddot{O}} - \ddot{S} = \underset{\cdot\cdot}{O}:$$

Ans. $:\underset{\cdot\cdot}{\ddot{O}} - \ddot{S} = \underset{\cdot\cdot}{O}:$

Formal charge on atom

$$= \text{No. of valence electrons} - \text{No. of non-bonding electrons} - \frac{1}{2}\text{ No. of bonding electrons}$$

FC on S atom $= 6 - 2 - ½ (6) = +1$
FC on double bonded O atom $= 6 - 4 - ½ (4) = 0$
FC on single bonded O atom $= 6 - 6 - ½ (2) = -1$

So, we may write :

$$:\overset{-1}{\underset{\cdot\cdot}{\ddot{O}}} - \overset{+1}{\ddot{S}} = \overset{0}{\underset{\cdot\cdot}{O}}:$$

Q. 10. Identify the compound/compounds in which S does not obey octet rule:
SO_2, SO_3, SF_4, SF_6, SF_2, H_2S

Ans. SF_4, SF_6

Q. 11. How is lattice enthalpy related to stability of an ionic compound?

Ans. Larger the lattice enthalpy of an ionic compound larger is its stability.

Q. 12. Give one example of a molecule not obeying octet rule.

Ans. PF_5

BOND PARAMETERS

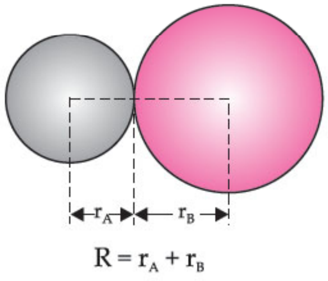
Covalent bonds are characterised by certain parameters such as bond length, bond angle and bond energy.

1. Bond length

Bond length is defined as

the equilibrium distance between the centres of the nuclei of two bonded atoms in a molecule.

Therefore, *it represents equilibrium internuclear separation distance of the bonded atoms in a molecule.*



It is measured by spectroscopic, X-ray diffraction and electron diffraction techniques. Each atom of the bonded pair contributes to bond length. In the case of a covalent bond, the contribution from each atom is called the **covalent radius** of that atom. The bond length in a covalent molecule AB may be expressed as

$$R = r_A + r_B$$

where R is the bond length and r_A and r_B are the covalent radii of atoms A and B respectively. Thus, the bond length is approximately the sum of the covalent radii of two atoms. For example, the O — H bond length in ethanol is the sum of the covalent radii of H and O, *i.e.* 37 + 74 = 111 pm. It is usually expressed in Angstrom units (Å) or picometers (pm).

1 Å = 10^{-10} m and 1 pm = 10^{-12} m.

The covalent radius is measured approximately as the radius of an atom's core which is in contact with the core of an atom in a bonded situation. As already studied in Unit 3, covalent radius is half of the distance between two similar atoms joined by a covalent bond in the same molecule. On the other hand, the **van der Waals radius** represents the overall size of the atom which includes its valence shell in a nonbonded situation. ***Van der Waals radius*** *is* ***one half of the distance between two similar adjacent atoms belonging to two nearest neighbouring molecules of the same substance in the solid state.*** Covalent and van der Waals radii of chlorine are shown in Fig. 2.

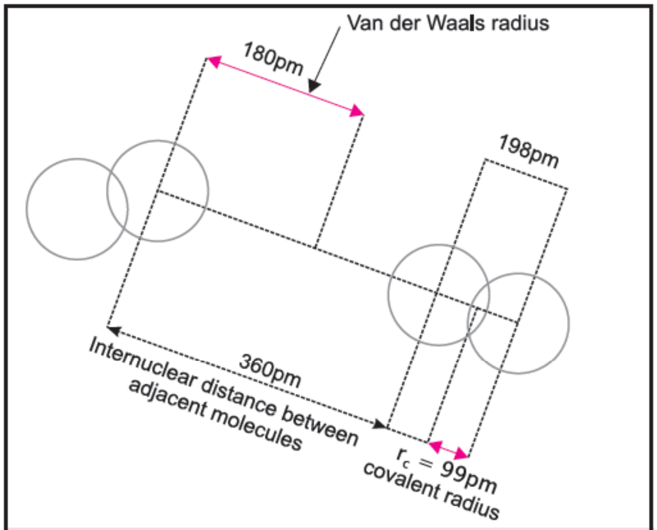


Fig. 2. Covalent and van der Waals radii of chlorine.

It is clear from Fig. 2., the internuclear distance between two atoms of the same molecule is 198 pm so that

$$r_{\text{covalent}} = \frac{198}{2} = 99 \text{ pm.}$$

The internuclear distance between two non-bonded nearest neighbouring atoms is 360 pm so that

$$r_{\text{van der Waals}} = \frac{360}{2} = 180 \text{ pm}$$

The van der Waals radii are always larger than covalent radii.

The average bond lengths for some single, double and triple bonds are given in Table 3 and the bond lengths for some common molecules are given in Table 4.

Table 3. Average bond lengths of some common bonds (single, double and triple) (pm).

Bond	Bond Length
O—H	96
C—H	107
C—N	143
C—C	154
Si—Si	234
Ge—Ge	244
N—O	136
$C = C$	134
$C = N$	138
N=O	122
$C \equiv C$	120
$C \equiv N$	116

Table 4. Bond length in some common molecules (pm).

Molecule	Bond Length
H_2(H—H)	74
F_2(F—F)	144
Cl_2(Cl—Cl)	198
Br_2(Br —Br)	228
I_2(I—I)	267
HF(H—F)	92
HCl(H—Cl)	127
HBr(H—Br)	141
HI(H—I)	160
$N_2(N \equiv N)$	109
$O_2(O = O)$	121

Factors affecting bond length

Bond length depends upon the following factors :

***(i)* Bond multiplicity**

Bond length decreases with increase in bond multiplicity. Thus, $C \equiv C$ bond length is shorter than $C = C$ bond which in turn is shorter than C—C bond,

i.e., $C \equiv C < C = C < C — C$.

Similarly,

$N \equiv N < N = N < N — N$ and $O = O < O — O$.

***(ii)* Size of the atom**

The bond length increases with increase in the size of the atoms. It is also clear from the table that the bond lengths for a given family increase with increase in atomic number. For example,

C — C < Si — Si < Ge — Ge

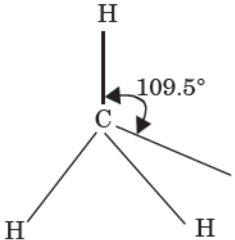
This is expected because with the increase in size of the atom, the distance of the valence electrons from the nucleus increases successively with the addition of a new shell. Consequently, the distance between the bonding nuclei (bond length) increases.

2. Bond angle

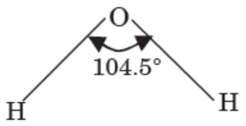
Bond angle may be defined as

the average angle between the orbitals containing bonding electron pairs around the central atom in a molecule.

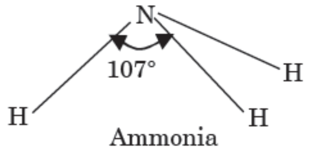
It is expressed in degree/minute/second. Bond angle gives an idea about the distribution of orbitals around the central atom in a molecule and therefore, determines the shape of a molecule. For example, the H—C—H bond angle in methane is 109.5°, the H—O—H bond angle in H_2O is 104.5° and H—N—H bond angle in ammonia is 107°.



Methane



Water



Ammonia

3. Bond enthalpy

We have learnt that when a bond is formed between the atoms, energy is released. This means that the bonded atoms have lesser energy than the separated individual atoms. Obviously, the same amount of energy will be needed to break the bond. This is called **bond dissociation enthalpy** and is measure of *bond strength*. **Bond dissociation enthalpy** may be defined as

> ***the amount of energy required to break one mole of bonds of a particular type between the atoms in the gaseous state.***

It is generally expressed in terms of kJ mol^{-1}. For example, the bond dissociation enthalpy of H—H bond in hydrogen molecules is 435.8 kJ mol^{-1}.

$$H_2(g) \longrightarrow H(g) + H(g) \quad \Delta_a H° = 435.8 \text{ kJ mol}^{-1}$$

Similarly, the bond dissociation enthalpy of Cl—Cl in Cl_2 is 242.5 kJ mol^{-1}, I—I in I_2 is 151 kJ mol^{-1} and H—I in HI is 298.3 kJ mol^{-1}, etc. Similarly, for molecules containing double bond (O_2) and triple bond (N_2), bond dissociation enthalpies are :

$$O_2\ [O=O]\ (g) \longrightarrow O\ (g) + O\ (g)\ \Delta_a H° = 498.0 \text{ kJ mol}^{-1}$$

$$N_2\ [N \equiv N]\ (g) \longrightarrow N\ (g) + N\ (g)\ \Delta_a H° = 946.0 \text{ kJ mol}^{-1}$$

It may be noted that larger the bond dissociation enthalpy, stronger will be the bond in the molecule. The bond dissociation enthalpy of some simple bonds are given in Table 5.

Table 5. Bond dissociation enthalpy of some common bonds.

Bond	Bond dissociation enthalpy (kJ mol^{-1})
H—H	435.8
H—Cl	431.7
H—Br	366.1
H—I	298.3
F—F	158.1
Cl—Cl	243.5
Br—Br	192.8
I—I	151.0
N—H	389.2
O—H	464
O═O	498
C—H	414
C—C	433
C ═ C	619
C ≡ C	836
N ≡ N	946.0

Bond dissociation enthalpy depends upon two factors :

(*i*) **Size of the bonded atoms :** The smaller the size of the bonded atoms, the stronger is the bond. consequently, larger is the value of bond dissociation enthalpy. For example, the bond dissociation enthalpy of H—H bond (435.8 kJ mol^{-1}) is larger than the bond dissociation enthalpy of Cl—Cl bond (243.5 kJ mol^{-1}).

(*ii*) **Bond length :** Shorter the bond length, larger is the value of bond enthalpy. For example, C—C bond length (154 pm) is larger than C = C bond length (134 pm). Consequently, the bond dissociation enthalpy of C—C bond (433 kJ mol^{-1}) is smaller than that of C = C bond (619 kJ mol^{-1}).

Average bond enthalpy : Bond dissociation enthalpy of polyatomic molecules

In the case of polyatomic molecules (which contain more than one bond of the same type), the average of the bond enthalpies of the bonds are taken. The average of the bond dissociation enthalpies is called **average bond enthalpy** or simply as **bond enthalpy.** For example, in the case of water molecule, the enthalpy needed to break the two O–H bonds is not the same.

$$H_2O\ (g) \longrightarrow H\ (g) + OH\ (g) \qquad \Delta_a H_1° = 502 \text{ kJ mol}^{-1}$$

$$OH\ (g) \longrightarrow H\ (g) + O\ (g) \qquad \Delta_a H_2° = 427 \text{ kJ mol}^{-1}$$

The difference in the $\Delta_a H°$ values suggests that the second O–H bond undergoes some change because of the changed chemical environment. This is the reason for some difference in energy of same O–H bond in different molecules such as CH_3OH (methanol), C_2H_5OH (ethanol), water, etc. Therefore for polyatomic molecules, mean or average bond enthalpy is used. It is obtained as the average of the different bond dissociation enthalpies in a molecule. For example, for water,

$$\text{Average bond enthalpy} = \frac{502 + 427}{2}$$
$$= 464.5 \text{ kJ mol}^{-1}$$

Thus bond enthalpy is the average enthalpy required to break bonds of a given type in one mole of the gaseous molecules. Obviously, for diatomic molecules, the bond dissociation enthalpy is same as bond enthalpy.

4. Bond order

The bond order is defined as *the number of bonds between two atoms in a molecule.* For example, bond order in H_2 (with a single shared electron pair) is one, in O_2 (with two shared electron pairs) is two and in N_2 (with three shared electron pairs) is three.

H : H Bond order = 1
O ∷ O Bond order = 2
N ⋮⋮ N Bond order = 3
C ⋮⋮ O Bond order = 3

It may be noted that **isoelectronic species** (molecules and ions) have same bond order. For example,

F_2, O_2^{2-} (18 electrons) have bond order 1

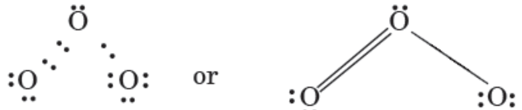
N_2, CO and NO^+ (14 electrons) have bond order = 3

It may be remembered that in general,

- **With increase in bond order, bond enthalpy increases and bond length decreases.**

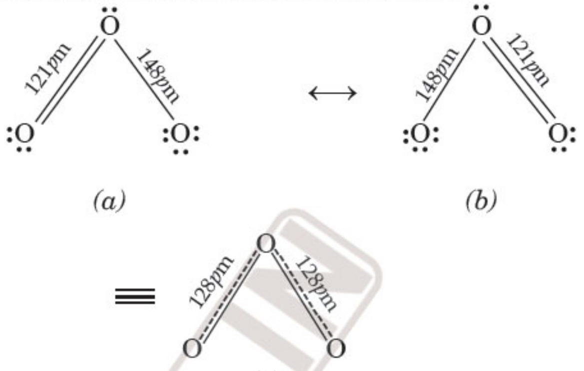
RESONANCE

The phenomenon of resonance was put forward by Heisenberg to explain the properties of certain molecules. It is often observed that a single Lewis structure is not adequate for the representation of a molecule in agreement with its experimentally determined parameters. To illustrate this consider a molecule of ozone (O_3). Its structure can be written as:



In this case, each oxygen atom has an octet of electrons. According to this structure, there is one single bond (O – O) and one double bond (O = O) in the molecule. The normal O–O and O=O bond lengths are 148 pm and 121 pm respectively. According to the above structure we would expect the two bond lengths in ozone molecule to be unequal. However, experimentally it is observed that both the bond lengths are equal (128 pm) and the bonds are intermediate between single and double bonds. This means that the above Lewis structure does not account for the observed experimental facts. To solve the problem, an alternative structure may be drawn as :

In this case, the double bond and the single bond are interchanged. But none of these two structures explains the observed facts. It is proposed that the actual structure is in between the two structures. In such a case, we say that the actual structure is a resonance hybrid of these two structures. The individual structures are called **resonance structures** or **contributing structures**. These are represented by drawing double headed arrows between these structures as shown below :



(*a*) (*b*)

(*c*)

Thus, **resonance** may be summed up as :

> ***when a molecule cannot be represented by a single structure but its characteristic properties can be described by two or more than two structures, then the actual structure is said to be a resonance hybrid of these structures.***

For example, ozone molecule may be represented as a resonance hybrid of above two structures (*a*) and (*b*). For simplicity, ozone may be represented by structure (*c*) which shows the resonance hybrid having equal bonds between single and double.

Conditions for Writing Resonance Structures

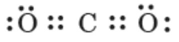
The following are essential conditions for writing resonating structures :

1. The contributing structures should have same atomic positions.
2. The contributing structures should have same number of unpaired electrons.
3. The contributing structures should have nearly same energy.
4. The structures should be so written that negative charge is present on an electronegative atom and positive charge is present on an electropositive atom.
5. In contributing structures, the like charges should not reside on adjacent atoms.

The contributing structures should not differ much in energy. This is an important condition. The individual structures of similar energy contribute equally to the resonance hybrid.

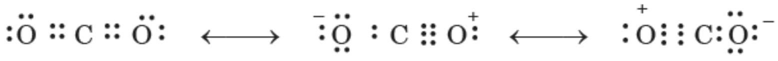
Let us discuss some other molecules :

(*i*) **Carbon dioxide molecule.** The simple structure of carbon dioxide molecule is



Therefore, we expect a double bond between carbon and oxygen atoms. The experimentally determined carbon to oxygen bond length in CO_2 molecule is 115 pm. The normal C = O bond length is 122 pm and C ≡ O bond length is 110 pm. This suggests that carbon-oxygen bond in CO_2 molecule is between double and triple bond.

Obviously, a single structure cannot depict the true structure of the molecule and it becomes necessary to write more than one Lewis structures. Therefore, the structure of CO_2 is best described as a resonance hybrid of the following three canonical forms :

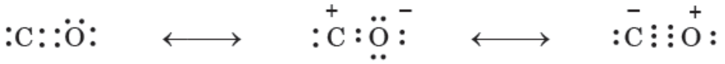


I II III

(*ii*) **Carbon monoxide molecule, CO.** The simple structure of carbon monoxide may be written as :

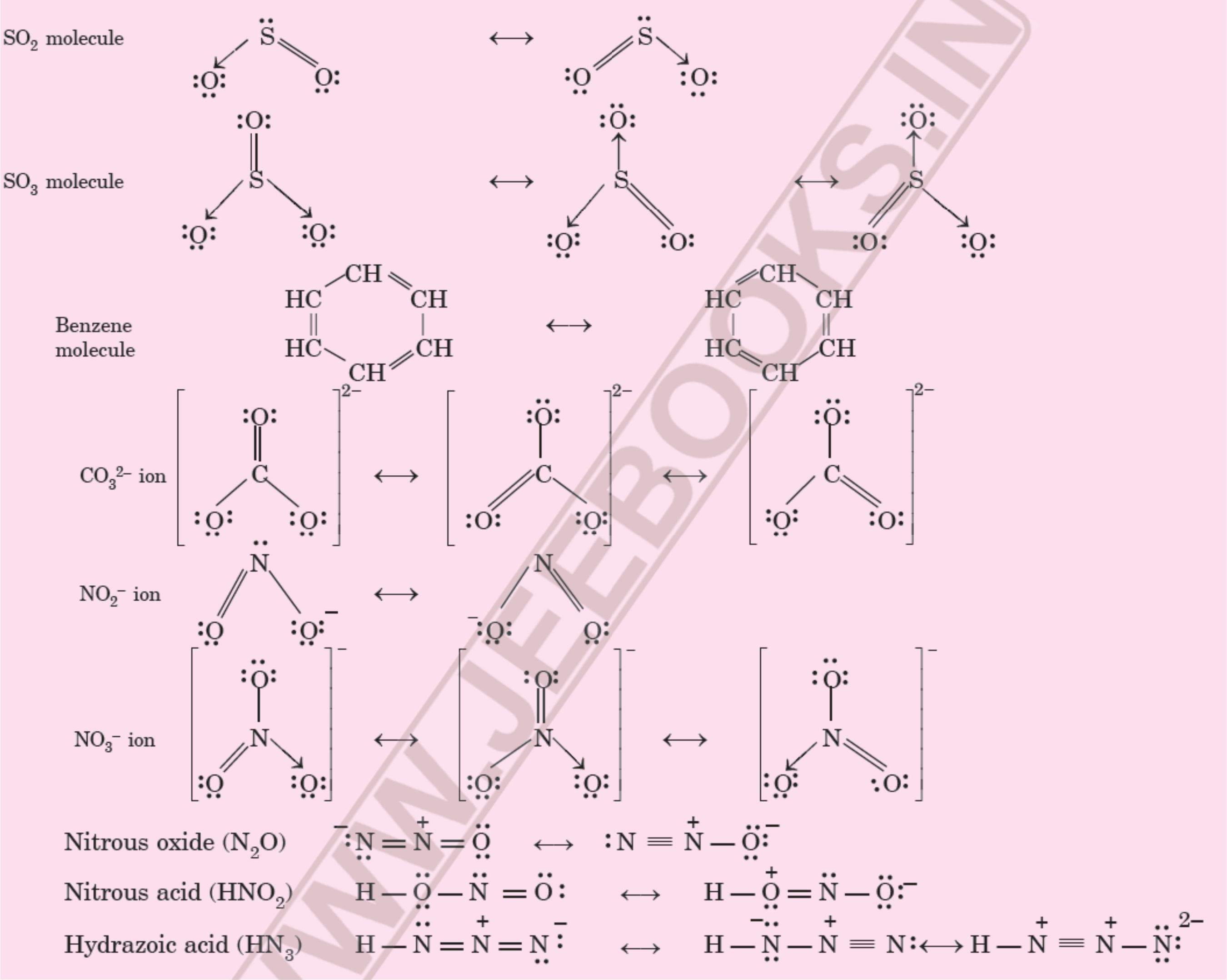
$$:C::\underset{..}{O}:$$

Therefore, we expect a double bond in carbon and oxygen atoms. However, carbon-oxygen bond length has been experimentally determined to be 113 pm. This lies between normal C = O (122 pm) and C ≡ O (1.10 pm). Therefore, carbon monoxide has been proposed to be resonance hybrid of the following structures :



$$:C::\ddot{O}: \longleftrightarrow :\overset{+}{C}:\underset{..}{\ddot{O}}\overset{-}{:} \longleftrightarrow :\overset{-}{C}\vdots\vdots\overset{+}{O}:$$

The resonance structures of a few more molecules and ions are given ahead.



Nitrous oxide (N_2O) $\quad \overset{-}{:\underset{..}{N}}=\overset{+}{N}=\ddot{\underset{..}{O}} \longleftrightarrow :N\equiv\overset{+}{N}-\ddot{\underset{..}{O}}\overset{-}{:}$

Nitrous acid (HNO_2) $\quad H-\ddot{\underset{..}{O}}-\ddot{N}=\ddot{O}: \longleftrightarrow H-\overset{+}{\underset{..}{O}}=\ddot{N}-\ddot{\underset{..}{O}}:^{-}$

Hydrazoic acid (HN_3) $\quad H-\ddot{N}=\overset{+}{N}=\underset{..}{\overset{-}{N}}: \longleftrightarrow H-\underset{..}{\overset{-}{N}}-\overset{+}{N}\equiv N: \longleftrightarrow H-\overset{+}{N}\equiv\overset{+}{N}-\underset{..}{\ddot{N}}:^{2-}$

Thus, we may conclude

- Resonance averages the bond characteristics of a molecule as a whole.
- Resonance stabilizes the molecule because the energy of the resonance hybrid is less than the energy of any single canonical structure.

Resonance energy. It is the difference between the actual bond energy of the molecule and that of the most stable of the resonating structures (having least energy). Thus,

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

For example, the resonance energy of carbon dioxide is 138 kJ mol^{-1}. This means that the actual molecule of CO_2 is about 138 kJ more stable than the most stable structure among the contributing structures. This can be easily illustrated as given below :

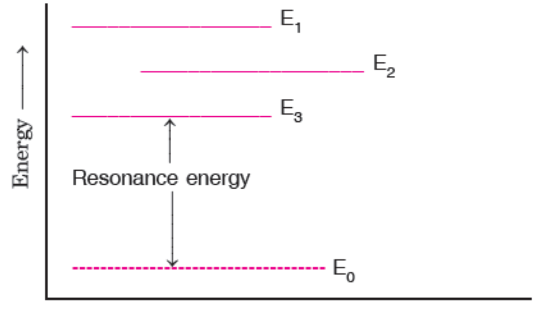


Fig. 3. Concept of resonance energy. Energies E_1, E_2 and E_3 are for three structures and E_0 is the experimentally determined bond energy.

Suppose E_1, E_2 and E_3 are the energies of three resonating structures for a molecule. Their energies are shown in Fig. 3. It is evident that among these, E_3 has the lowest energy (most stable contributing structure). If E_0 is the actual energy of the molecule (experimentally determined), then resonance energy is $E_3 - E_0$.

Characteristics of Resonance

1. The contributing structures do not have real existence. These are only imaginary proposed to explain the properties of the molecule. Only the resonance hybrid has the real existence.
2. Because of resonance, the bond lengths in a resonating structures become equal. For example, both the O—O bond lengths in O_3 are equal. All the C–C bonds in benzene are equal.
3. The resonance hybrid has lower energy and thus greater stability than any of the contributing structures.
4. Greater is the resonance and resonance energy, greater is the stability of the molecule.
5. Concept of resonance is a theoretical concept.

Calculation of Bond Order for Molecules Showing Resonance

In case of molecules or ions showing resonance, the contribution of each structure should be counted towards bond order. The bond order may be calculated as:

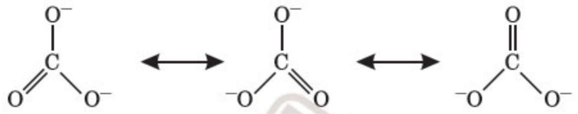
$$\text{Bond order} = \frac{\text{Total number of bonds between two atoms in all the structures}}{\text{Total number of resonating structures}}$$

Any two bonded atoms may be selected and a double bond is counted as 2 bonds and a triple bond is counted as 3 bonds.

For example, benzene has two structures having a double bond and a single bond between two carbon atoms.

$$\text{Bond order} = \frac{2+1}{2} = 1.5$$

Carbonate ion, CO_3^{2-} has three resonating structures as:



$$\text{Bond order of C and O} = \frac{2+1+1}{3} = 1.33$$

➢ Some misconceptions

There are certain misconceptions about resonance. The following points should be kept in mind :

⇒ The resonating structures (canonical forms) have no real existence.

⇒ It does not mean that the molecule exist for a certain fraction of time in one canonical form and for other fraction of time in another canonical form.

⇒ There is no equilibrium between the canonical forms like tautomeric forms (Keto-enol forms) in tautomerism.

⇒ The real molecule cannot be depicted by a single Lewis structure.

POLARITY OF BONDS

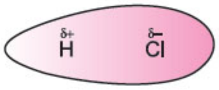
The existence of a hundred percent ionic bond or a covalent bond represents an ideal situation. However, in reality no bond is completely covalent or completely ionic. Even in the case of covalent bond between two hydrogen atoms, there is some ionic character.

When a covalent bond is formed between two similar atoms, the shared pair of electrons is equally attracted by the two atoms. As a result of this, the electron pair is situated exactly in between two identical nuclei as shown below :

$$\mathrm{H : H} \qquad \mathrm{:\ddot{\underset{..}{Cl}} : \ddot{\underset{..}{Cl}}:} \qquad \mathrm{:\ddot{\underset{..}{F}} : \ddot{\underset{..}{F}}:}$$

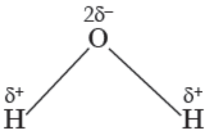
The common examples are H_2, O_2, N_2, Cl_2, F_2, etc. The bond is known as *non-polar covalent bond.* On the other hand, if the atoms forming bonds are different, the electron attracting powers of the two atoms in a bond may differ. Consequently, the shared pair will be displaced towards the atom having more electronegativity. We have learnt in previous unit that, the electronegativity measures the tendency of an atom to attract the shared pair of electrons towards itself in a covalent bond. For example, let us consider a molecule of HCl. The electronegativities of Cl and H are 3.0 and 2.1 respectively. Due to the larger electronegativity of chlorine, the bonding pair will be attracted more towards chlorine atom. Therefore, chlorine atom will experience more negative charge around it and the other atom will experience as if it has lost some of its negative charge. Due to this, the chlorine end of the molecule will acquire *slightly negative charge* and the hydrogen end will have *slightly positive charge*. These are represented as δ – and δ+ (delta meaning small) charges. Such molecules having two oppositely charged poles are called **polar molecules** and the bond is said to be **polar covalent bond.** The magnitude of electronegativity difference reflects the degree of polarity. *Greater the difference in the electronegativities of the atoms forming the bond, greater will be the charge separation and hence greater will be the polarity of the molecule.*

$\mathrm{H} : \ddot{\underset{\cdot\cdot}{\mathrm{Cl}}} :$



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

Similarly, molecules such as BrCl, H_2O, HF, etc. are also polar molecules.



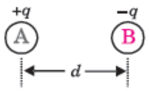
Dipole Moment—A Measure of Degree of Polarity

As studied above, in the case of polar molecules, the centre of negative charge does not coincide with the centre of positive charge. Such molecules having two equal and opposite charges separated by certain distance are said to possess **electric dipole**. For example, a molecule like HCl behaves like a dipole. Since the molecule as a whole is electrically neutral, the negative charge is always equal to the positive charge. The degree of polarity in the molecule is expressed by a term known as dipole moment. **Dipole moment** is defined as

> ***the product of the magnitude of the charge and the distance of separation between the charges.***

It is usually represented by a Greek letter 'μ'. Mathematically,

dipole moment = charge (q) × distance of separation



or $\mu = q \times d$

where q = charge on any of the atoms

d = distance between the atoms

Since the charge 'q' is of the order of 10^{-10} e.s.u and the intermolecular distance 'd' is of the order of 10^{-8} cm (*i.e.*, 1Å), therefore, the dipole moment 'μ' is of the order of $10^{-10} \times 10^{-8}$ *i.e.*, 10^{-18} esu cm. This quantity is called 1 Debye and is denoted by the symbol 'D'. Thus,

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

For example, dipole moment of HCl molecule is 1.03 D and that of H_2O is 1.85 D.

In SI units, dipole moment is expressed in the units of Cm; as

$$1\ \text{esu} = \frac{1.602 \times 10^{-19}\text{C}}{4.803 \times 10^{-10}} = 3.335 \times 10^{-10}\text{C}$$

$$\text{and}\quad 1\ \text{cm} = 10^{-2}\ \text{m}$$

$$\begin{aligned} 1\ \text{D} &= 10^{-18}\ \text{esu cm} \\ &= 10^{-18}(3.335 \times 10^{-10}\text{C}) \times (10^{-2}\ \text{m}) \\ &= \mathbf{3.335 \times 10^{-30}\ Cm} \end{aligned}$$

Dipole moment is a vector quantity and is represented by a small arrow with tail at the positive centre and head pointing towards the negative centre.

+ (end) ⟶ – (end)

For example, the dipole of HCl may be represented as :

The shift in electron density is symbolised by crossed arrow (+⟶) above the Lewis structure to indicate the direction of the shift.

Dipole Moment and Molecular Structure

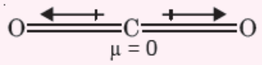
(*a*) Diatomic molecules. A diatomic molecule has two atoms bonded to each other by a covalent bond. In such a molecule, the dipole moment of the bond (known as bond dipole) also gives the dipole moment of the molecule. Thus, a diatomic molecule is polar, if the bond formed between the atoms is polar. For example, dipole moment of HCl molecule is the same as that of H—Cl bond, (μ = 1.07 D).

Greater the electronegativity difference between the atoms, more will be the dipole moment of such molecules. For example, the dipole moment of hydrogen halides decreases with decreasing electronegativity of the halogen atom.

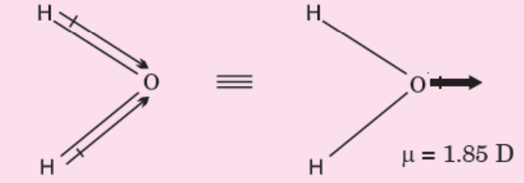
	H—F	H—Cl	H—Br	H—I
Electronegativity of halogen atom	4.0	3.0	2.8	2.5
Dipole moment	1.78 D	1.07 D	0.79 D	0.38 D

(*b*) Polyatomic molecules. In case of polyatomic molecules (containing more than two atoms), the dipole moment not only depends upon the individual dipole moments of the bonds (called bond dipoles) but also on the spatial arrangement of the various bonds in the molecule. In such cases, the dipole moment of a molecule is the vector sum of the dipole moments of various bonds. For example, carbon dioxide (CO_2) and water (H_2O) are both triatomic molecules but dipole moment of carbon dioxide is zero whereas, that of water is 1.84 D. This can be explained on the basis of their structures.

Carbon dioxide is a linear molecule in which the two C ═O bonds are oriented in the opposite directions at an angle of 180°. The dipole moment of each C ═ O bond is 2.3 D but due to linear geometry of CO_2, the dipole moment of one C ═ O bond cancels that of another. Therefore, the resultant dipole moment of the molecule is zero.



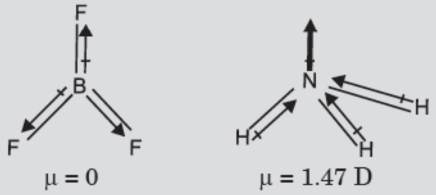
Hence, CO_2 is a non-polar molecule. On the other hand, water molecule has a bent structure in which the two O—H bonds are oriented at an angle of 104.5°. The dipole moment of water is 1.85 D (or 1.85 × 3.335 × 10^{-30} Cm = 6.17 × 10^{-30} Cm) , which is the resultant of the dipole moments of two O—H bonds.



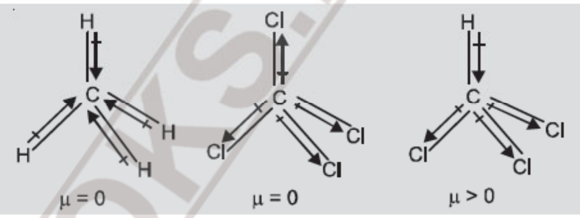
Bond dipoles   Resultant dipole moment

The dipole moment in case of BeF_2 is zero. This is because the molecule is linear and the two equal bond dipoles point in opposite directions. These bond dipoles cancel the effect of each other giving a net zero dipole moment.

Let us consider tetra-atomic molecules such as BF_3 and NH_3. The dipole moment of BF_3 molecule is zero while that of NH_3 is 1.47 D or 4.90 × 10^{-30} Cm. This suggests that BF_3 molecule has symmetrical structure in which the three B—F bonds are oriented at an angle of 120° to one another. The three bonds lie in one plane and the dipole moments of these bonds cancel one another giving net dipole moment equal to zero. On the other hand, the ammonia molecule has pyramidal structure. The individual bond dipole moments of three N—H bonds give the resultant dipole moment of NH_3 molecule as 1.47 D.



Thus, it may be concluded that *the presence of polar bonds in a polyatomic molecule does not mean that the molecule as a whole will always have dipole moment*. In some cases, the arrangement of individual bonds in the molecule is such that the net dipole moment of the molecule is zero. For example, as discussed earlier, the net dipole moments of carbon dioxide and boron trifluoride molecules are zero. Similarly, the dipole moments of methane and carbon tetrachloride molecules are zero because of the symmetrical tetrahedral shapes of these molecules. However, the dipole moment of $CHCl_3$ (chloroform) is not zero because all the bonds are not same. The resultant of bond dipole moments of three C—Cl bonds is not cancelled by bond dipole moment of C—H bond.



R.U. Curious...

❑ NH_3 and NF_3 molecules present an interesting case in relation to net dipole moment

▶ Both these molecules have pyramidal shape with one lone pair on nitrogen atom. Fluorine is more electronegative than hydrogen and therefore, the N–F bonds should be more polar than N–H bonds. Consequently, the resultant dipole moment of NF_3 should be much larger than that of NH_3. However, the dipole moment of ammonia (μ = 1.47 D) is larger than that of NF_3 (μ = 0.24 D). The anomalous behaviour can be explained due to the presence of lone pair on nitrogen. In case of NH_3, nitrogen is more electronegative than H [electronegativity of N(3.0) and of H(2.1)] and therefore, the dipole of N–H bond is from H to N. The orbital dipole due to lone pair is in the same direction as the resultant dipole moment of the three N–H bonds. Therefore, it adds on the resultant dipole moment of the N–H bonds. On the other hand, in case of NF_3, fluorine is more electronegative than nitrogen [electronegativity of F(4.0) and of N(3.0)] and therefore, the dipole of N–F bond is from N to F. The orbital dipole is in the opposite direction to the resultant dipole moment of the three N–F bonds. Thus, the lone pair moment cancels the resultant N–F bond moments as shown in figure. Consequently, the dipole moment of NF_3 is low.

μ = 1.47 D (or 4.90 × 10^{-30} Cm)   μ = 0.24 D (or 0.80 × 10^{-30} Cm)

The dipole moments of some molecules are given in Table 6.

Table 6. Dipole moments of some molecules.

Type of molecule	Example	Dipole moment μ (D)	Geometry
AB	HF	1.78	Linear
	HCl	1.07	Linear
	HBr	0.79	Linear
	HI	0.38	Linear
	H_2	0	Linear
AB_2	H_2O	1.85	Bent
	H_2S	0.95	Bent
	CO_2	0	Linear
	BeF_2	0	Linear
	CS_2	0	Linear
AB_3	NH_3	1.47	Trigonal pyramidal
	NF_3	0.24	Trigonal pyramidal
	BF_3	0	Trigonal planar
AB_4	CH_4	0	Tetrahedral
	$CHCl_3$	1.04	Tetrahedral
	CCl_4	0	Tetrahedral

Importance of Dipole Moment

Dipole moment plays very important role in understanding the nature of chemical bond. A few applications are given below :

***(i)* Distinction between polar and non-polar molecules.** The measurement of dipole moment can help us to distinguish between polar and non-polar molecules. Non-polar molecules have zero dipole moment while polar molecules have some value of dipole moment. For example, H_2 molecule with zero dipole moment is non-polar molecule while HCl molecule having dipole moment of 1.07 D is a polar molecule. Some other examples are given below :

Non-polar molecules (Dipole moment = 0)		Polar molecules	
H_2	CO_2	H_2O	1.85 D
O_2	BeF_2	HF	1.78 D
Cl_2	BF_3	HCl	1.07 D
N_2	CH_4	H_2S	0.95 D

***(ii)* Degree of polarity in a molecule.** Dipole moment measurement also gives an idea about the degree of polarity specially in a diatomic molecule. The greater the dipole moment, the greater is the polarity in such a molecule. For example, HF (1.78 D) is more polar than HCl (1.07 D).

***(iii)* Shapes of molecules.** As already discussed, in case of molecules containing more than two atoms, the dipole moment not only depends upon the individual dipole moments of the bonds but also on the arrangement of bonds. Thus, dipole moment is used to find the shapes of molecules. For example, the dipole moment of water is 1.85 D while that of carbon dioxide is zero. This means that carbon dioxide is a linear molecule in which the individual dipole moments of two CO bonds cancel each other. On the other hand, water is not linear but it has angular shape as shown above, having the resultant dipole moment of two bond dipoles as 1.84 D.

(iv)* Ionic character in a molecule.** Knowing the electronegativities of atoms involved in a molecule, it is possible to predict the nature of chemical bond formed. If the difference in electronegativities of two atoms is large, the bond will be highly polar. As an extreme case, when the electron is completely transferred from one atom to another, an ionic bond is formed. Therefore, the ionic bond is regarded as an extreme case of covalent bond. The greater the difference in electronegativities of the bonded atoms, the higher is the ionic character. It has been observed that ***when the electronegativity difference between two atoms is 1.7, then the bond is 50% ionic and 50% covalent. If the electronegativity difference is more than 1.7, then the chemical bond formed is predominantly ionic (more than 50% ionic character) and if the difference is less than 1.7, the bond formed is mainly covalent. Larger the electronegativity difference, larger will be the ionic character. For example, bond between Cs (0.7) and F (4.0) is more ionic than bond between Li (1.0) and F (4.0). On the other hand, the bond between C (2.5) and H (2.1) or Cl (3.0) is almost covalent because the electronegativity difference between bonding atoms is small.

The percentage of ionic character can be calculated from the ratio of the observed dipole moment to the dipole moment for the complete electron transfer (100% ionic character). For example, in HCl molecule, the observed dipole moment is 1.07 D and its bond length is 1.275 Å. Assuming 100% ionic character, the charge developed on H and Cl atoms would be 4.8×10^{-10} esu. Therefore, dipole moment for 100% ionic character will be

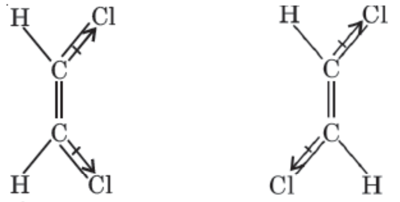
$$\mu_{\text{ionic}} = q \times d = 4.8 \times 10^{-10} \text{ esu} \times 1.275 \times 10^{-8} \text{ cm}$$
$$= 6.12 \times 10^{-18} \text{ esu cm} = 6.12 \text{ D}$$
$$(1 \text{ D} = 10^{-18} \text{ esu cm})$$

$\therefore$ % ionic character

$$= \frac{\text{Observed dipole moment}}{\text{Dipole moment for complete ionic character}} \times 100$$

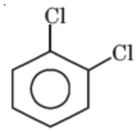
$$= \frac{1.07}{6.12} \times 100 = 17.48\%$$

***(v)* Distinguish between cis- and trans-isomers.** Dipole moment measurements help to distinguish between *cis-* and *trans-* isomers because cis- isomer has usually higher dipole moment than trans isomer. For example, in trans-isomer of 1, 2-dichloroethene, the dipole moment is less because the bond moments of C—Cl bonds cancel each other.

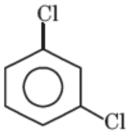


cis ($\mu \neq 0$) trans ($\mu = 0$)

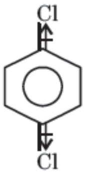
***(vi)* Distinguish between *ortho, meta* and *para* isomers.** Dipole moment measurements help to distinguish between *o-*, *m-* and *p-* isomers because the dipole moment of *p*-isomer is zero and that of *o*-isomer is more than that of m-isomer. For example, for dichlorobenzene :



ortho
μ = 2.54 D



meta
μ = 1.48 D

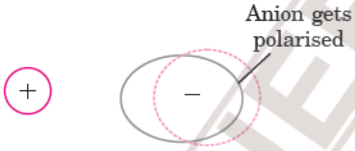


para
μ = 0

Partial Covalent Character in Ionic Bonds

Ionic and covalent bonds are two extreme types of bonds. In fact, most of the heteronuclear bonds have intermediate character. Even in the case of pure ionic compounds, there is some degree of covalent character. When two oppositely charged ions A^+ and B^- are brought together, the positive ion attracts the outermost electrons of the negative ion. This results in distortion of electron clouds around the anion towards the cation. ***This distortion of electron cloud of the negative ion by the positive ion is called* polarisation**. If the polarisation is small, the bond is mainly ionic. On the other hand, if the degree of polarisation is large, electron cloud is drawn more from the negative ion to the positive ion. Consequently, the charges on the ions become less (negative becomes less, +ve charge also becomes less because some of it is neutralised by the electron cloud of anion). This decreases the ionic character of the bond and favours the covalent character. The polarisation of an anion by cation is shown below. In Fig. (a), the two ions are shown without any polarisation, assuming that the bond is completely ionic. This represents an ideal ion pair. The positive ion polarises the negative ion and draws electrons towards itself. As a result of polarisation, there is decrease of positive charge on the cation and decrease of negative charge on the anion. This leads to **covalent character**. Obviously, **if polarisation is more, larger will be covalent character of the bond**. Thus, the type of bond depends upon the degree of polarisation.

(*a*)



(*b*)

- *If there is no polarisation, the bond is mainly ionic.*
- *If the degree of polarisation is small, the bond will be ionic with some covalent character and*
- *If the polarisation is more, the covalent character becomes predominent.*

The extent of polarisation depends on both the ions as :

(*i*) *the power of the cation to distort or polarise the anion.*

(*ii*) *the susceptibility of the anion to get polarised by the cation.*

The tendency of the cation to polarise and the polarisability of the anion are summarised in the following rules known as **Fajan rules**.

Fajan Rules

1. Small size of the cation. *Smaller the size of the cation, greater is its polarising power.* The polarising power of a cation decreases with increase in its size. The small cations have high electron density and therefore, they tend to distort or polarise the electron cloud of the anion to greater extent. Therefore, the compounds containing small cations will have more covalent character. This easily explains that LiCl is more covalent than NaCl and KCl.

2. Large size of anion. *Polarisation increases with increase in size of anion*. This is because the electron cloud on the bigger anion will be held less firmly by its nucleus and, therefore, would be more easily deformed towards the cation. Thus, larger the anion, the higher will be its polarisability and more will be covalent character in its compounds. Therefore, the anions such as I^-, Br^-, S^{2-}, Se^{2-}, etc. are easily polarisable and have larger tendency to induce covalent character in ionic compounds.

Therefore, covalent character of lithium halides follows the order : Li I > Li Br > Li Cl > Li F

3. Large charge on cation or anion. *Larger the charge on cation greater is polarising power and larger the charge on anion greater is its tendency to get polarised.* For example, Na^+ and Ca^{2+} have almost similar ionic radii but $CaCl_2$ has higher covalent character than NaCl because of higher charge on Ca^{2+} ion. Consequently the melting point of $CaCl_2$ is less than that of NaCl.

Compound	Radius	m.pt (°K)
NaCl	Na^+ : 0.95 Å	1073
$CaCl_2$	Ca^{2+} : 0.99 Å	1045

4. Electronic configuration of the cation : Cations with 18 electrons shell configuration (known as *pseudo inert gas configuration*) cause greater polarisation than the cations with 8 electrons shell configuration with the same size and charge. This is due to the fact that in case of 18 electrons shell ion, there are 10 *d* electrons in addition to eight *s*-and *p*–electrons. The d-electrons donot shield the nuclear charge effectively and therefore, they have increased effective nuclear charge. Consequently, these ions behave as though they are under the influence of greater nuclear charge and polarise the anion to a greater extent. Therefore, such compounds will have more covalent character.

For example, if we compare the ions of same size; Na^+ and Cu^+, Na^+ has eight electrons shell configuration ($2s^2 2p^6$) while Cu^+ has 18 electrons shell configuration ($3s^2\ 3p^6\ 3d^{10}$). The Cu^+ ion polarize the anion more than Na^+ ion. As a result, copper chloride, CuCl is slightly covalent and therefore, insoluble in water whereas NaCl is ionic and highly soluble in water. The covalent character of CuCl in comparison to NaCl is also supported by its low melting point. Melting point of CuCl is 705 K while that of NaCl is 1073 K.

Thus, according to Fajan rules, the covalent character will be favoured by :

(*i*) Small size of cation

(*ii*) Large size of anion

(*iii*) High charge of cation and anion

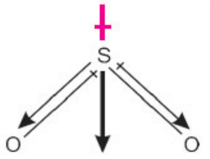
(*iv*) The cation having 18-electrons shell.

SOLVED EXAMPLES

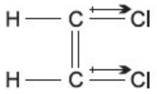
❑ **Example 8.**

Sketch the bond moments and resultant dipole moments in
(i) SO_2 (ii) cis-and trans of $C_2H_2Cl_2$

Solution: (*i*)

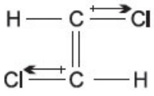


(*ii*) *cis* –



Resultant $\mu \neq 0$

trans –



Resultant $\mu = 0$

❑ **Example 9.**

Calculate the percentage ionic and covalent character of HF molecule having bond distance = 0.92 Å and dipole moment = 1.78 D

Solution:

Dipole moment of the molecule assuming 100% ionic character :

$$\mu_{\text{ionic}} = q \times r$$
$$q = 4.8 \times 10^{-10} \text{ esu}, \quad r = 0.92 \times 10^{-8} \text{cm}$$
$$\mu_{\text{ionic}} = 4.8 \times 10^{-10} \times 0.92 \times 10^{-8}$$
$$= 4.416 \times 10^{-18} \text{ esu cm} = 4.416 \text{ D}$$

Observed dipole moment, $\mu_{\text{observed}} = 1.78$ D

Percentage ionic character

$$= \frac{\mu_{\text{observed}}}{\mu_{\text{ionic}}} = \frac{1.78}{4.416} \times 100 = \mathbf{40.3\ \%}$$

Percentage covalent character $= 100 - 40.3$

$$= \mathbf{59.7\ \%}$$

❑ **Example 10.**

The dipole moment of HBr molecule is 0.78 D and the bond distance is 1.41 Å. Calculate the fractional charges δ on H and Br atoms in HBr (electronic charge, $e = 4.8 \times 10^{-10}$ esu).

Solution: Dipole moment, $\mu = q \times r$

$\mu = 0.78 \text{ D} = 0.78 \times 10^{-18}$ esu. cm,

$r = 1.41 \times 10^{-8}$ cm

$$\therefore \quad q = \frac{0.78 \times 10^{-18} \text{ esu cm}}{1.41 \times 10^{-8} \text{ cm}} = 0.55 \times 10^{-10} \text{ esu.}$$

Now, fraction of charge = $\dfrac{\text{Charge present}}{\text{Electronic charge}}$

$$\delta = \frac{q}{e} = \frac{0.55 \times 10^{-10}}{4.8 \times 10^{-10}} = 0.11$$

$$\therefore \quad \boldsymbol{\delta_{H^+} = 0.11, \quad \delta_{Br^-} = -0.11}$$

❑ **Example 11.**

The dipole moment of lithium hydride is 1.962×10^{-29} cm and interatomic distance between Li and H in the molecule is 0.1592 nm. Calculate the percentage ionic character of the molecule.

Solution: Dipole moment of the molecule assuming 100% ionic character,

$$\mu_{\text{ionic}} = q \times d$$
$$q = 1.602 \times 10^{-19}\text{C}, \ d = 0.1592 \text{ nm}$$
$$= 0.1592 \times 10^{-9} \text{ Cm}$$
$$\therefore \quad \mu_{\text{ionic}} = (1.602 \times 10^{-19} \text{ C}) \times (0.1592 \times 10^{-9} \text{ m})$$
$$= 2.55 \times 10^{-29} \text{ Cm}$$
$$\mu_{\text{observed}} = 1.962 \times 10^{-29} \text{ Cm}$$
$$\therefore \quad \% \text{ ionic character } = \frac{\mu_{\text{ observed}}}{\mu_{\text{ ionic}}} \times 100$$
$$= \frac{1.962 \times 10^{-29} \text{Cm}}{2.55 \times 10^{-29} \text{ Cm}} \times 1000$$
$$= \mathbf{76.94\%}$$

Practice Problems

- **11.** Which molecule is polar in each of the following pairs ?

(*i*) HF, F_2	(*ii*) CO_2, H_2O
(*iii*) N_2, NH_3	(*iv*) CH_4, CH_3Cl.

- **12.** Which of the following hydrogen halides has the most polar bond ?

(*i*) HF	(*ii*) HCl
(*iii*) HBr	(*iv*) HI.

- **13.** Which of the following molecules have electric dipoles ?

(*i*) CCl_4 (*ii*) $CHCl_3$ (*iii*) CH_2Cl_2
(*iv*) CH_3Cl (*v*) CH_4.

- **14.** Predict the dipole moment of :
  - (*i*) a molecule of the type AX_2 having a linear geometry.
  - (*ii*) a molecule of the type AX_4 having tetrahedral geometry.
  - (*iii*) a molecule of the type AX_2 having angular geometry.
  - (*iv*) a molecule of the type AX_4 having square planar geometry.

Answers to Practice Problems

- **11.** (*a*) HF (*b*) H_2O (*c*) NH_3 (*d*) CH_3Cl
- **12.** (*a*) HF
- **13.** $CHCl_3$, CH_2Cl_2, CH_3Cl
- **14.** (*i*) zero (*ii*) zero (*iii*) appreciable dipole moment (*iv*) zero

GEOMETRY OR SHAPES OF MOLECULES

The different atoms in a molecule have definite geometric arrangements in space around the central atom. ***This definite relative arrangement of the bonded atoms in a molecule*** is known as the **geometry** or **shape of the molecules.**

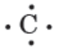
VALENCE SHELL ELECTRON PAIR REPULSION (VSEPR) THEORY

In 1940, Sidgwick and Powell proposed a simple theory based on the repulsive interactions of the electron pairs in the valence shell of the atoms. It was further developed and refined by Nyholm and Gillespie in 1957. They suggested that the shapes of molecules can be determined by the number of electron pairs (bonding as well as non-bonding) in the valence shell of the central atom and proposed a theory known as **valence shell electron pair repulsion (VSEPR) theory**. The basic idea of this theory is that *bonded atoms in a molecule adopt that particular arrangement in space around the central atom which keeps them on an average as far apart as possible.*

Postulates of VSEPR Theory. The main postulates of VSEPR theory are :

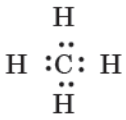
1. The shape of a molecule depends upon the number of valence shell electron pairs (whether bonded or not) around the central atom.

In the formation of a bond, the central atom shares its valence electrons with the surrounding atoms. However, in certain cases, all the valence shell electrons may not take part in the bond formation. The electrons left in the valence shell without forming bonds exist as **lone pairs**. For example, in methane, (CH_4), carbon uses all the four valence electrons in forming four bond pairs. On the other hand, in water (H_2O), the central oxygen atom has ($1s^2\,2s^2 2p^4$) six valence electrons. The hydrogen atom shares two of these six valence electrons in bond formation leaving four electrons as two lone pairs. Thus, in methane, there are four bond pairs around carbon, while oxygen in water has two bond pairs and two lone pairs around it.

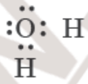


(Four valence electrons)

(Six valence electrons)



(Four bond pairs)



(Two bond pairs and two lone pairs)

2. Electron pairs in the valence shell tend to repel one another because their electron clouds are negatively charged.

3. The electron pairs tend to occupy positions in space that minimize repulsions. Therefore, they *try to stay as far apart as possible to acquire a state of minimum energy or maximum stability.*

4. The valence shell is taken as a sphere with the electron pairs localizing on the spherical surface at maximum distances from one another.

5. The electron pairs in multiple bonds are treated as a single unit like a single electron pair. In other words, two or three electron pairs of a double bond or a triple bond respectively are considered as a single super pair equivalent to a single electron pair.

6. Repulsion between the lone pair and lone pair of electrons is different than that between two bond pairs or one lone pair and one bond pair. The repulsive interactions decrease in the order :

Lone pair — Lone pair > Lone pair — Bond pair > Bond pair —Bond pair.

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

7. Repulsive forces decrease sharply with increasing angle between the electron pairs. They are strong at 90°, weaker at 120° and weakest at 180°.

Nyholm and Gillespie (1957) improved VSEPR model by pointing to the important difference between lone pairs and bond pairs. They suggested that the repulsive interactions between the bonded and the lone pairs of electrons are different. This can be understood as follows :

The orbital of bonded electron pair is under the influence of two nuclei and most of the electron cloud is oriented between the nuclei of the two atoms. On the other hand, the lone pair of electrons is under the influence of only one nucleus and, therefore, its electron cloud is spread out and tends to occupy more space. For example, Fig. 4 shows a molecule of ammonia (NH_3) in which there are three bond pairs and one lone pair. Since the lone pair is flatter and occupies more space around the central atom, it can interact more and, therefore, it will repel the electron pairs in the neighbouring orbitals strongly than do the electrons in the bonded orbital. Obviously, the repulsion between two lone pairs would be the largest and will be lesser if one of them is bond pair and the least if both are bond pairs.

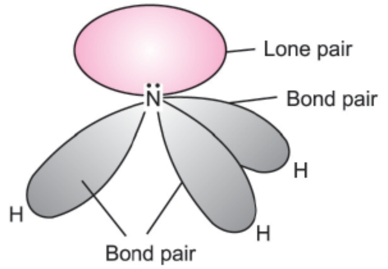


Fig. 4. Lone pair and bond pairs in NH_3 molecule.

Thus, *the repulsive interactions between different pairs of electrons* will decrease in the order :

Lone pair—Lone pair > Lone pair—Bond pair > Bond pair—Bond pair

Shapes of molecules on the basis of VSEPR theory

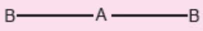
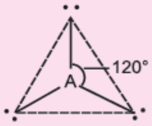
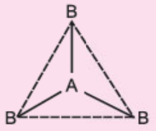
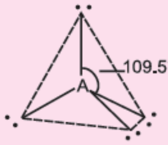
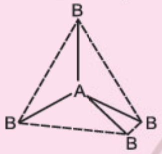
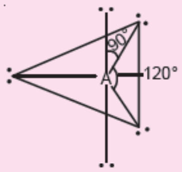
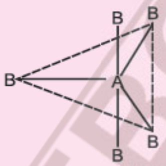
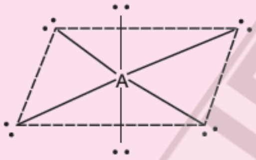
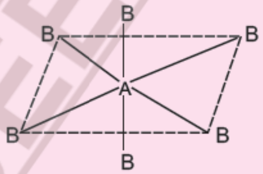
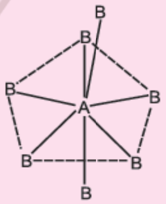
This theory is very simple to use. *In this theory no distinction is made between s-and p-electrons. We take into account only the number of electron pairs present in the valence shell of the central atom.* Thus, the particular geometry of a molecule depends upon the number of electron pairs around the central atom. For example, if there are two electron pairs around the central atom, the only way to keep them as far apart as possible is to arrange them at an angle of 180° to each other. The molecule in such a case will adopt **linear** geometry.

Similarly, for three electron pairs around the central atom, the molecule adopts **trigonal planar** geometry and for four electron pairs around the central atom, the molecule adopts **tetrahedral** geometry.

The molecules having five electron pairs around the central atom have **trigonal bipyramidal** geometry. The molecules having six electron pairs around the central atom have **octahedral** geometry.

The goemetries of molecules based on the number of electron pairs is given in Table 7.

Table 7. Geometries of molecules on the basis of VSEPR theory.

Number of electron pairs around central atom	Arrangement of electron pairs	Molecular Geometry	Bond angles	Examples
2		Linear 	180°	BeF_2, $BeCl_2$, BeH_2, $ZnCl_2$
3		 Trigonal planar	120°	BF_3, $AlCl_3$
4		 Tetrahedral	109.5°	CH_4, SiH_4, SiF_4, NH_4^+
5		 Trigonal bipyramidal	three 120° two 90°	PF_5, $SbCl_5$
6		 Octahedral	90°	SF_6, TeF_6
7		 Pentagonal bipyramidal	90°, 72°	IF_7

Let us illustrate this theory by considering a few examples :

A. Shapes of Molecules containing Bond Pairs only

1. Shape of BeF_2 molecule : Linear

In BeF_2, the central Be-atom (Z = 4; $1s^2\ 2s^2$) has two electrons in the valence shell. In the formation of BeF_2, each of these valence electrons is shared by two flourine atoms. As a result, the Be-atom is surrounded by two bond pairs of electrons [Fig. 5]. Therefore, the geometry of BeF_2 molecule is **linear** as shown and the bond angle is 180°.

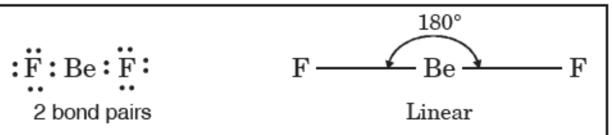


Fig. 5. Shape of BeF_2 molecule having two electron pairs around Be-atom.

Other molecules such as $BeCl_2$, $ZnCl_2$, $HgCl_2$ have linear shape.

2. Shape of BF_3 molecule : Trigonal planar

The central atom, boron (Z = 5, $1s^2\ 2s^2\ 2p^1$) has *three valence electrons*. In the formation of BF_3

molecule, each electron in the valence shell of B-atom forms a bond pair with F-atom. As a result, the central boron atom is surrounded by three bond pairs and the molecule adopts **trigonal planar** geometry. In this geometry, all the F—B—F bond angles are of 120°. This geometry is planar because the three F-atoms and B-atom lie in the same plane.

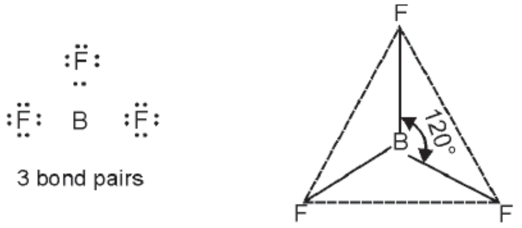


Fig. 6. Shape of BF_3 molecule having three electron pairs around B-atom.

Molecules such as BCl_3, $AlCl_3$, etc. have same shape.

3. Shape of CH_4 molecule : Tetrahedral

The central atom, carbon (Z = 6, $1s^2 2s^2 2p^2$) has four valence electrons. All the four valence electrons are bonded to four hydrogen atoms forming four bond pairs around the central carbon atom. These four electron pairs, trying to remain as far apart as possible, adopt **tetrahedral structure.** In this geometry, all the H—C—H bond angles are of 109°28′ (or approximately 109.5°).

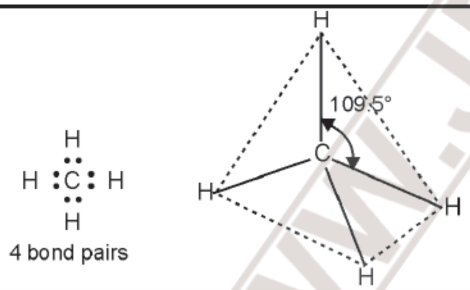


Fig. 7. Shape of CH_4 molecule having four electron pairs around C-atom.

Other examples of tetrahedral molecules are SiF_4, CCl_4, SiH_4, NH_4^+, etc.

4. Shape of PCl_5 molecule : Trigonal bipyramidal

In PCl_5, the central atom, P (Z = 15 ; $1s^2$, $2s^2 2p^6$, $3s^2 3p^3$) has five valence electrons. It forms five bond pairs with five Cl-atoms to form a molecule of PCl_5. Since there are five electron pairs around the central phosphorus atom and therefore, it has **trigonal bipyramidal** geometry as shown in Fig. 8. In this geometry, all the bond angles are not equal. Three electron pairs are in the same plane at an angle of 120°, while other two are perpendicular to the plane, both making an angle of 90° with the plane. Thus, in this arrangement three bond angles are of 120° each and two are of 90° each.

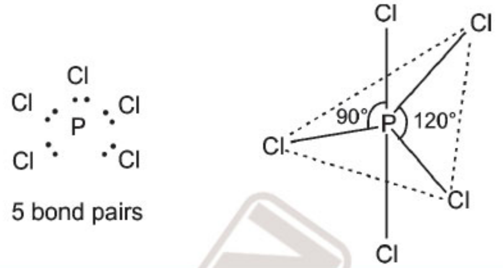


Fig. 8. Shape of PCl_5 molecule having five electron pairs around P-atom.

In this geometry, all five P—Cl bonds are not equal. The three bonds lying in the trigonal plane are called **equatorial bonds.** Of the remaining two bonds, one lies above and the other below the equatorial plane, both making an angle of 90° with the plane. These bonds are called **axial bonds.** It has been observed that axial bonds are slightly longer than equatorial bonds in this geometry. PF_5 has the same shape.

The larger bond length of axial bonds than equatorial bonds can be explained in terms of the repulsive forces between electron pairs due to different bond angles. Let us count the repulsive interactions of an axial and an equatorial electron pair. As shown in the figure (Fig. 9) the electron pair of axial bond (say 1) is being repelled by three electron pairs (of bonds 2,3 and 4) at 90° and one (of bond 5) at 180°. On the other hand, the electron pair of the equatorial bond (say 2) is being repelled by two electron pairs (1 and 5) at 90° and two (3 and 4) at 120°. Now, we know that the repulsion between electron pairs decreases with increasing angle between them. Therefore, the repulsion between electron pairs at 120° and 180° may be neglected in comparison to those at 90°. Thus, considering only the repulsions between electron pairs at 90°, we observe that each axial bond is repelled by three electron pairs while each equatorial bond is repelled by two bond pairs. This means that axial bond pair faces greater repulsion from other bonds and therefore, the axial bond is slightly longer than equatorial bond.

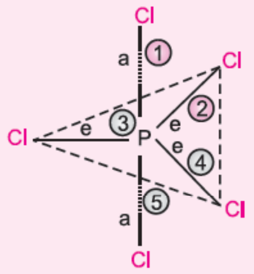


Fig. 9. Axial and equatorial bonds in PCl_5

It may be noted that the structure of PCl_5 molecule is unsymmetrical. As a result, it is less stable and is therefore, highly reactive.

5. Shape of SF_6 molecule : Octahedral.

In SF_6, the central S-atom (Z = 16 ; $1s^2\ 2s^2\ 2p^6$, $3s^2\ 3p^4$) has *six valence electrons*. Each of these six valence electrons forms bond with F-atom and therefore, the molecule has **octahedral geometry.** In this case, all the bond angles are same and are of 90° each. TeF_6 molecule has same shape.

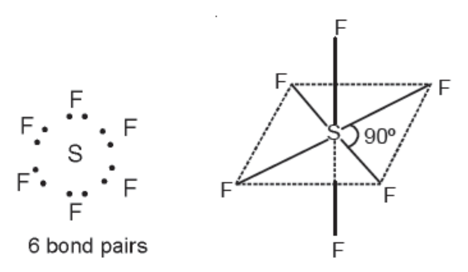


Fig. 10. Shape of SF_6 molecule having six electron pairs around S-atom.

Other examples of octahedral molecules are SeF_6, TeF_6, etc.

6. Shape of IF_7 molecule : Pentagonal bipyramidal

In IF_7, the central atom I (Z = 53, ... $5s^25p^5$) has *seven valence electrons*. Each of these seven valence electrons forms bond with F-atom and therefore, the molecule has **pentagonal bipyramidal geometry.** In this case, all the bond angles are not equal. Five electron pairs are in the same plane at an angle of 72°, while other two are perpendicular to the plane both making an angle of 90° with the plane. Thus, in this arrangement five bond angles are of 72° each and two are of 90° each.

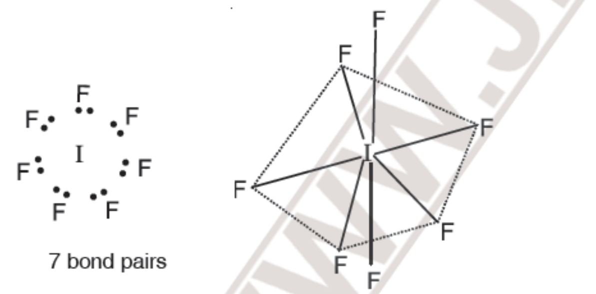


Fig. 11. Shape of IF_7 molecule having seven electron pairs around I atom.

B. Shapes of Molecules containing Lone Pairs and Bond Pairs

Now, let us consider a few molecules containing bond pairs as well as lone pairs.

1. Molecules containing three electron pairs (AB_3 or AB_2L)

If the valence shell of an atom contains three electron pairs, then the molecule has **trigonal planar geometry** (e.g., BF_3). However, if it contains a lone pair in addition to bond pair, the geometry gets distorted. For example, a molecule of the type AB_2L (where L represents a lone pair), has V-shaped geometry as discussed for SO_2 molecule.

Shape of sulphur dioxide (SO_2) molecule.

In SO_2 molecule, there are three electron pairs (two bond pairs and one lone pair).

The three electron pairs should acquire a trigonal planar arrangement with bond angle 120°. Since one of the positions is occupied by a lone pair, the geometry may be described as **angular** or **V-shaped** or **bent shape.**

Fig. 12. Shape of SO_2 molecule.

Now, lone pair-bond pair repulsion is more than bond pair-bond pair repulsion. Therefore, bonded pairs of electrons are pushed more closer and the OSO bond angle gets reduced to 119.5° from the value of 120°.

2. Molecules Containing Four Electron Pairs (AB_4, AB_3L, AB_2L_2)

As already learnt, the molecule AB_4 has **tetrahedral** geometry. But if lone pairs are also present in addition to bond pairs, the geometry gets distorted. This may be illustrated by taking two examples :

(*a*) Molecules containing 3 *bp* and 1 *lp* AB_3L. *e.g.*, NH_3

(*b*) Molecules containing 2 *bp* and 2 *lp* AB_2L_2 *e.g.*, H_2O.

(*a*) Molecules containing 3 *bp* and 1 *lp*; AB_3L.

Shape of NH_3 (ammonia) molecule

In ammonia molecule, the central nitrogen atom (Z = 7, $1s^2\ 2s^2\ 2p^3$) has five valence electrons. Three of these valence electrons share electrons with three hydrogen atoms forming three bond pairs around the nitrogen atom. The remaining two electrons are present as a lone pair. Thus, in ammonia, nitrogen is surrounded by **four electron pairs** (three bond pairs and one lone pair). These four electron pairs adopt **tetrahedral geometry.** But all the four electron pairs around nitrogen are not equivalent (three bond pairs and one lone pair) and therefore, ammonia has *distorted tetrahedral* geometry. The bond angle will not be 109.5° but it is 107°. This distortion is due to the presence of one lone pair in addition to bond pairs. As already explained, lone pair-bond pair repulsion is more than bond pair-bond pair repulsion. As a result, the lone pair of electrons will repel the bond pairs strongly and bond angle decreases to 107°. The geometry of ammonia molecule is also regarded as **pyramidal** (Fig. 13).

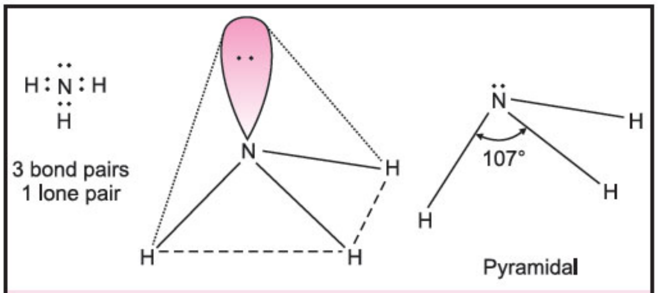


Fig. 13. Shape of NH_3 molecule according to VSEPR theory.

Other molecules with same shape are PCl_3, NF_3, H_3O^+, etc.

(*b*) Molecules containing 2 *bp* and 2 *lp*; AB_2L_2

Shape of H_2O (water) molecule

In the case of water molecule, the central oxygen atom (Z = 8, $1s^2\, 2s^2\, 2p^4$) has six valence electrons. In the formation of water molecule, the electrons form two bond pairs with two hydrogen atoms leaving four electrons as two lone pairs.

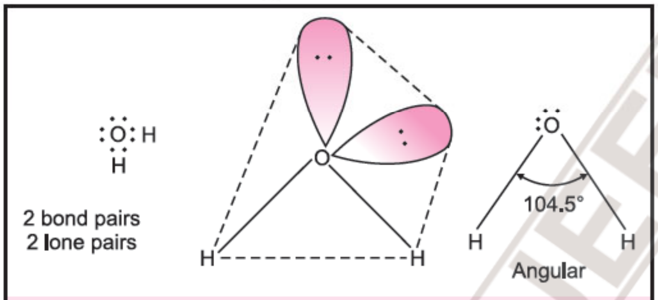


Fig. 14. Shape of H_2O molecule according to VSEPR theory.

The four electron pairs around the central oxygen atom adopt tetrahedral geometry. However, all the four electron pairs around O are not equivalent and therefore, geometry is *distorted tetrahedral*. The bond angle in water molecule is not of 109.5° but it is of 104.5° (Fig. 14). The distortion is due to the presence of two lone pairs in addition to bond pairs. The force of repulsion between lone pair–lone pair is larger than the force of repulsion between two bond pairs of electrons. Thus in water, the two lone pairs of electrons move away from each other while the two O—H bonds are forced closer to each other (even more than N—H bonds in NH_3) resulting in decrease of H—O—H angle to 104.5°. The resulting geometry is regarded as **bent** or **angular.** Other molecules with same shape are H_2S, F_2O, SCl_2, etc.

KEY NOTE

It may be noted here that the central atoms (C, N and O) in three molecules CH_4, NH_3 and H_2O have four electron pairs around the central atom. Therefore, these molecules adopt tetrahedral geometries. But in methane, there is no lone pair, NH_3 molecule has one lone pair while H_2O molecule has two lone pairs in the total of four electron pairs. Due to the presence of lone pairs, NH_3 and H_2O molecules will have distorted geometries, while CH_4 molecule will have regular geometry of tetrahedron. Due to larger lone pair–bond pair repulsion than bond pair–bond pair in NH_3, the bond angle is reduced from 109.5° to 107°. The geometry of NH_3 is **pyramidal.**

Now, in case of H_2O, two lone pairs force the O—H bonds more closely than the N–H bonds in NH_3. So the bond angle decreases to a larger extent *i.e.*, to 104.5°. The geometry of water is regarded as **V-shaped** or **angular**.

3. Molecules Containing Five Electron Pairs (AB_5, AB_4L, AB_3L_2 or AB_2L_3)

When the central atom is surrounded by five electron pairs, the geometry is **trigonal bipyramidal.** However, if one or more bond pairs are replaced by lone pairs, the geometry gets distorted. This may be illustrated by the following examples :

(*a*) Molecules containing 4 *bp* and 1 *lp*. *e.g.*, SF_4.

(*b*) Molecules containing 3 *bp* and 2 *lp*. *e.g.*, ClF_3.

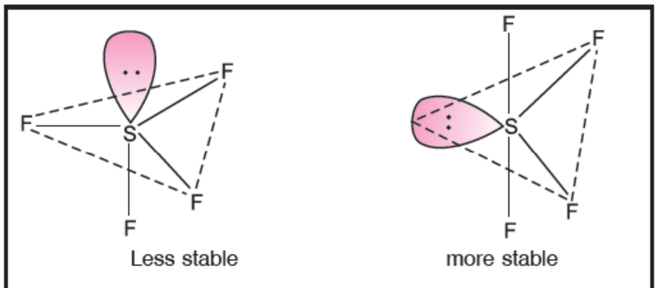
(*c*) Molecules containing 2 *bp* and 3 *lp*. *e.g.*, XeF_2.

(*a*) Molecules containing 4 *bp* and 1 *lp*; AB_4L

Shape of SF_4 (sulphur tetrafluoride) molecule

In this case, sulphur atom (Z = 16 : $3s^2\, 3p^4$) has six valence electrons. In the formation of SF_4, four electrons form four bond pairs and leave two electrons as one lone pair. Thus, five electron pairs around sulphur adopt trigonal bipyramidal geometry in which one position is occupied by a lone pair.

Therefore, SF_4 molecule can have structure *(a)* or structure *(b)* as shown in Fig 15, in which the lone pair is present on axial or equatorial positions respectively. Nyholm - Gillespie modification has helped in predicting accurately the geometry of such molecules containing lone pair of electrons.



(a) *lp* on axial position

(b) *lp* on equatorial position

Fig.15. Shape of SF_4 molecule.

In arrangement *(a)*, the lone pair is in on axial position which has 3 *lp*-*bp* repulsions at 90°. In structure *(b)* the lone pair is in on equatorial position and there are only two *lp*-*bp* repulsions. Hence arrangement *(b)* will experience lesser repulsions and will be stable in comparison to arrangement *(a)*. This shape is described as **distorted tetrahedron** or a **folded square** or a **see-saw.** The bond angles in SF_4 are 89° and 117° instead of 90° and 120° respectively.

(b) Molecules containing 3 *bp* and 2 *lp*; AB_3L_2

Shape of ClF_3 (chlorine trifluoride) molecule.

The central chlorine atom (Z = 17 : $3s^2\ 3p^5$) has seven electrons in its valence shell. In the formation of ClF_3, three electrons form three bond pairs and leave four electrons as two lone pairs. Thus, the five electron pairs around chlorine atom adopt trigonal bipyramidal geometry, in which two positions are occupied by lone pairs. As already discussed, the lone pair in trigonal bipyramidal geometry experiences more repulsions at axial positions, therefore, both the lone pairs are present at equatorial positions as shown in Fig. 16. The molecule is **T-shaped** and bond angle is 87.6° instead of 90°.

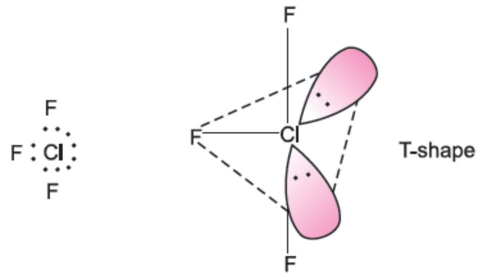
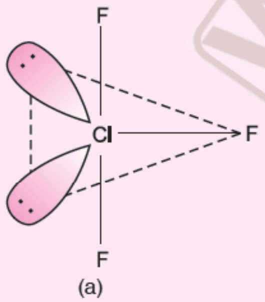


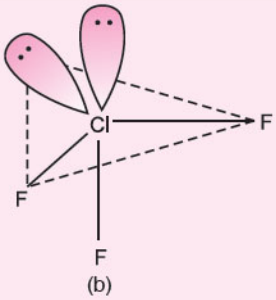
Fig. 16. Shape of ClF_3 molecule according to VSEPR theory.

KEY NOTE

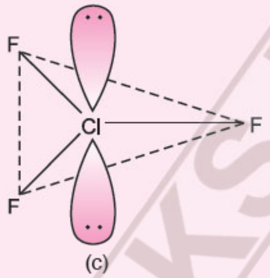
It may be noted that as in case of SF_4, the two lone pairs in ClF_3 may occupy the following three positions:



Two lone pairs on equatorial positions.
Repulsions at 90°
lp – *lp* =0, *lp* – *bp* =4,
bp – *bp* =2



One lone pair on axial and one lone pair on equatorial positions.
Repulsions at 90°
lp – *lp* =1, *lp* – *bp* = 3,
bp – *bp* =2



Two lone pairs on axial positions.
Repulsion at 90° :
lp – *lp* = 0, *lp* – *bp* = 6,
bp – *bp* = 0

It can be seen that **structure, (a) appears to be most stable because** in comparison to structure (b), it has no strong *lp* – *lp* repulsion and in comparison to structure (c), it has lesser number of *lp* – *bp* repulsions.

(c) Molecules containing 2 *bp* and 3 *lp*; AB_2L_3

Shape of XeF_2 (xenon difluoride) molecule.

Xenon atom has (Z = 54 : $5s^2\ 5p^6$) eight electrons in the valence shell. In the formation of XeF_2, there are two bond pairs and three lone pairs. These five electron pairs adopt trigonal bipyramidal geometry with three positions occupied by lone pairs. Since the three lone pairs are present at the corners of an equilateral triangle, the net repulsion on the bonds due to lone pairs is zero. Thus, the molecule has **linear geometry.**

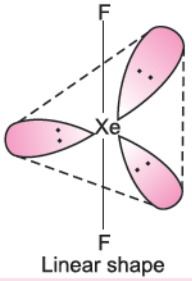


Fig. 17. Shape of XeF_2 molecule.

4. Molecules containing six Electron Pairs (AB_6, AB_5L, AB_4L_2)

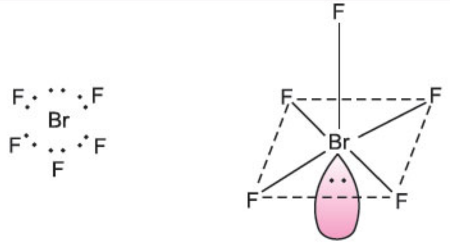
When the central atom is surrounded by six electron pairs, the geometry is octahedral. However, if one or more lone pairs are present in addition to bond pair, the geometry gets distorted. This may be illustrated by the following examples :

(a) Molecules containing 5 *bp* and 1 *lp e.g.,* BrF_5.
(b) Molecules containing 4 *bp* and 2 *lp e.g.,* XeF_4.

(a) Molecules containing 5 *bp* and 1 *lp*; AB_5L

Shape of BrF_5 (bromine pentafluoride) molecule

The central bromine atom (Z = 35, $4s^2\ 4p^5$) has seven valence electrons. In the formation of BrF_5, it has five bond pairs and one lone pair. The six electron pairs has octahedral geometry in which one of the positions is occupied by a lone pair. Since all the six positions in octahedral geometry are equivalent, therefore, lone pair may be placed on any position (Fig. 18).



Square pyramidal shape

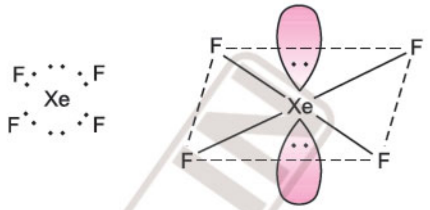
Fig. 18. Shape of BrF_5 molecule according to VSEPR theory.

The geometry of BrF_5 is termed as **square pyramidal.** IF_5 molecule has same geometry.

(*b*) Molecules containing 4bp and 2lp; AB_4L_2

Shape of XeF_4 (xenon tetrafluoride) molecule

In this case, the central xenon atom has eight electrons. In the formation of XeF_4, there are four bond pairs and two lone pairs. The six electron pairs has octahedral geometry (Fig. 19), in which two positions are occupied by lone pairs. The structure is termed as **square planar**.

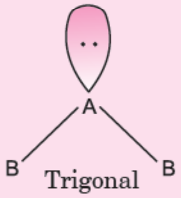
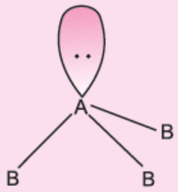
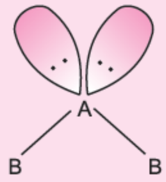
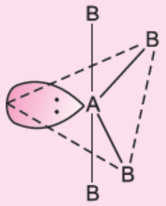


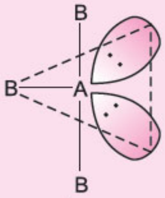
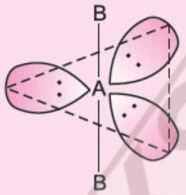
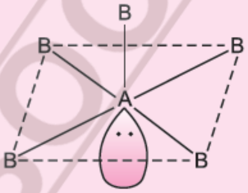
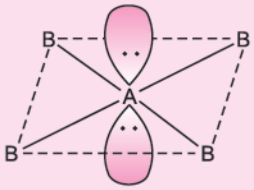
Square planar

Fig. 19. Shape of XeF_4 molecule according to VSEPR theory.

The shapes of some molecules according to VSEPR theory are summed up in Table 8.

Table 8. Shapes of some simple molecules or ions with central atom having one or more lone pairs of electrons.

Molecule type	No. of bonding pairs	No. of lone pairs	Total electron pairs	Arrangement of electron pairs	Shape (Geometry)	Example
AB_2L	2	1	3	 Trigonal planar	Bent or V shaped	SO_2, O_3, $SnCl_2$
AB_3L	3	1	4	 Tetrahedral	Pyramidal	NH_3
AB_2L_2	2	2	4	 Tetrahedral	V shaped	H_2O
AB_4L	4	1	5	 Trigonal bipyramidal	See saw	SF_4

AB_3L_2	3	2	5	 Trigonal bipyramidal	T shaped	ClF_3
AB_2L_3	2	3	5	 Trigonal bipyramidal	Linear	XeF_2
AB_5L	5	1	6	 Octahedral	Square pyramidal	BrF_5
AB_4L_2	4	2	6	 Octahedral	Square planar	XeF_4

Practice Problems

○ **15.** Arrange the following sets of molecules in the decreasing order of bond angle :

(i) SF_6, CCl_4, H_2O, NH_3

(ii) CH_4, NH_3, H_2O, BF_3

(iii) $AlCl_3$, H_2S, BeH_2, H_2O

○ **16.** Out of the following data assign the correct bond angle associated with each of the given compounds.

Compounds	*Bond angles*
H_2O, CO_2, CCl_4, BF_3	180°, 109°28′, 104.5°,
BeF_2, $AlCl_3$, PF_5, SF_6	107°, 120°, 90°
NH_3, CH_4	

○ **17.** Give one example each of molecules which have the following geometries ;

(a) Linear (b) Trigonal bipyramidal

(c) Tetrahedral.

Answers to Practice Problems

○ **15.** (i) CCl_4, (109.5°), NH_3(107°), H_2O(104.5°), SF_6(90°)

(ii) BF_3, (120°), CH_4(109.5°), NH_3(107°), H_2O(104.5°)

(iii) BeH_2, (108°), $AlCl_3$(120°), H_2S(104.5°), H_2S(100°)

○ **16.** $H_2O = 104.5°$, $CO_2 = 180°$, $CCl_5 = 109.5°$, $BF_3 = 120°$

$BeF_2 = 180°$, $AlCl_3 = 120°$ $PF_5 = 120°, 90°$, $SF_6 = 90°$

$NH_3 = 107°$, $H_2O = 104.5°$.

○ **17.** (a) BeF_2 (b) PF_5 (c) CH_4

VALENCE BOND APPROACH OF COVALENT BOND

The simple concept of covalent bond formation as a result of sharing of electrons does not provide any clue for the forces operating between atoms. It also does not give any reason for the difference in bond dissociation enthalpies and bond lengths in different molecules. For example, both H_2 and F_2 molecules have a single covalent bond formed by sharing of an electron pair between the respective atoms but they have quite different bond enthalpies and bond lengths as :

Molecule	H_2	F_2
Bond enthalpy	435.8 kJ mol^{-1}	150.6 kJ mol^{-1}
Bong length	74 *pm*	42 *pm*

The simple picture of covalent bonding also gives no idea about the shapes of polyatomic molecules. Similarly, the VSEPR theory gives the geometry of simple molecules but theoretically, it does not explain them and also has limited applications.

To overcome these limitations, two important theories based on quantum mechanical principles are commonly used. These are:

1. Valence bond (VB) theory
2. Molecular orbital (MO) theory

Let us briefly learn about these two theories.

Valence Bond theory

The valence bond theory was put forward by Heitler and London in 1927. It was later improved and developed by L. Pauling and J. C. Slater in 1931. The valence bond theory is based on the knowledge of atomic orbitals and electronic configurations of elements, overlap criteria of atomic orbitals and stability of molecule.

The **basic assumptions** of this theory are :

(*i*) Atoms do not lose their identity even after the formation of the molecule.

(*ii*) The bond is formed due to the interaction of only the valence electrons as the two atoms come close to each other. The inner electrons do not participate in the bond formation.

(*iii*) During the formation of bond, only the valence electrons from each bonded atom lose their identity. The other electrons remain unaffected.

(*iv*) The stability of bond is accounted by the fact that the formation of bond is accompanied by release of energy. The molecule has minimum energy at a certain distance between the atoms known as **internuclear distance**. Larger the decrease in energy, stronger will be the bond formed.

To understand the concept more clearly, let us consider the formation of H_2 molecule.

Valence Bond Treatment for H_2 Molecule

Consider two hydrogen atoms A and B approaching each other having nuclei H_A and H_B and the corresponding electrons e_A and e_B respectively. When the two atoms are at large distances from each other, no interaction between the two atoms takes place. At this stage, the total energy of the system is the sum of the energies of the individual atoms. When the two atoms come closer, new attractive and repulsive forces begin to operate. Besides the attraction of the nucleus of one atom for its own electrons *i.e.* $H_A–e_A$ and $H_B–e_B$, the following attractive and repulsive forces start operating :

(i) Attractive forces. Attractive forces operate between electron of atom A (e_A) and nucleus of B (H_B) and electron of atom B (e_B) and nucleus of A (H_A). These two new attractive forces are shown in Fig. 20 (*a*).

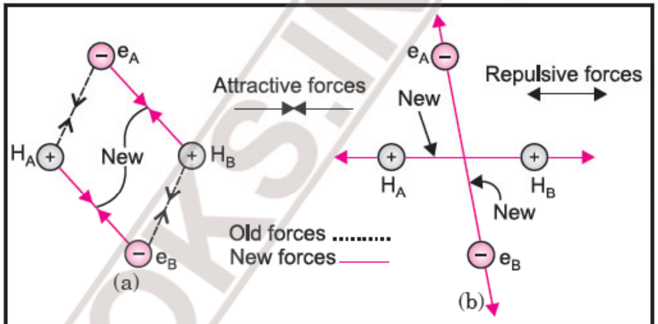


Fig. 20. (*a*) Attractive and (*b*) repulsive forces during formation of H_2 molecule.

***(ii)* Repulsive forces.** Repulsive forces are present between the nuclei $H_A–H_B$ and electrons of two atoms $e_A–e_B$. These two forces are shown in Fig. 20 (*b*).

Thus, the forces operating in the molecule are :

Attractive :

(*i*) Nucleus of one atom and its own electron

$H_A – e_A$ and $H_B – e_B$

(*ii*) Nucleus of one atom and electron of other atom:

$H_A – e_B$ and $H_B – e_A$

Repulsive :

(*i*) Electrons of two atoms :

$e_A – e_B$

(*ii*) Nuclei of two atoms :

$H_A – H_B$

Now we know that attractive forces tend to bring the atoms closer while repulsive forces tend to push them apart. *It has been observed experimentally that the magnitude of the new attractive forces is more than the new repulsive forces.* As a result, the two atoms approach each other (Fig. 21) and the potential energy of the system decreases. This situation has been shown in Fig. 21 (*b*) where the two atoms are close together. As the two atoms come closer and closer, the system becomes more and more stable due to decrease of energy. Ultimately, a stage is reached where the total forces of attraction balance the forces of repulsion and the system acquires minimum energy. This is shown in Fig. 21 (*c*). At this stage, the two hydrogen atoms are said to be bonded together to form a stable molecule and the distance (r_0) between the atoms is known as **bond length**. For hydrogen molecule, the distance between two hydrogen atoms corresponding to minimum energy is 74 *pm*. The potential energy of the system when two atoms are brought closer and

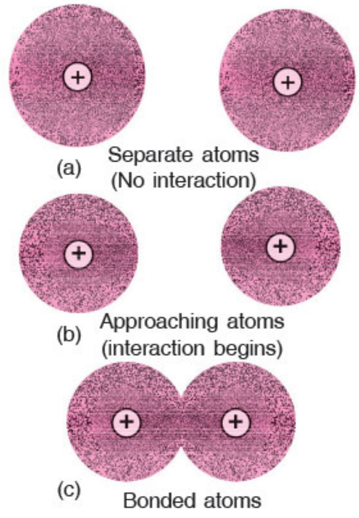


Fig. 21. Formation of hydrogen molecule when two hydrogen atoms approach each other.

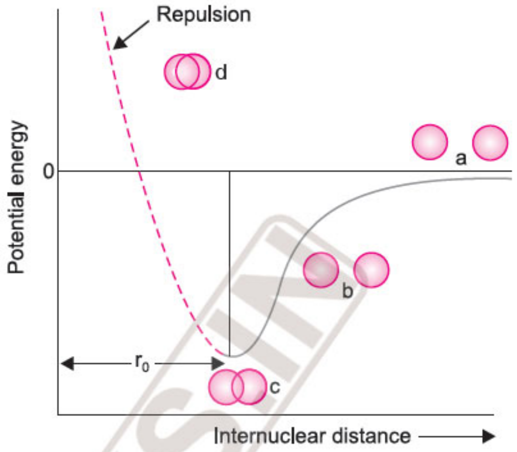


Fig. 22. Change of potential energy as two hydrogen atoms are brought closer and closer.

closer is represented in Fig. 22. This is called potential energy diagram. In this diagram, when the two atoms are for apart (stage *a*), there is no attractive or repulsive interactions between them and the potential energy of the system (isolated atoms) is assumed to be zero.

Thus, when the bond is formed, energy is released and therefore, the hydrogen molecule is more stable than the individual hydrogen atoms. That is,

$$\text{H} + \text{H} \longrightarrow \text{H}_2 + 435.8 \text{ kJ mol}^{-1}$$

This energy corresponding to minimum in the curve is called **bond energy.**

Conversely, when one mole of H_2 molecules is dissociated to hydrogen atoms, 435.8 kJ of energy is needed.

$$\text{H}_2\text{ (g)} + 435.8 \text{ kJ mol}^{-1} \longrightarrow \text{H (g)} + \text{H (g)}$$

It may be remembered that the two hydrogen atoms cannot be brought closer than 74 pm* because then the repulsive forces will become large and the potential energy would rise [stage(*d*) shown by dotted line in Fig. 22].

Why is helium molecule, He_2 not formed ? Now let us understand as to why He_2 molecule is not formed. This can be easily understood by calculating the attractive and repulsive forces when two helium atoms approach each other. Each helium atom has two electrons in its 1*s*-orbital. There are two attractive forces between the nucleus and the electrons of each atom. These are shown by dotted lines in Fig. 23 (*a*). It has been found that when two helium atoms approach each other, *four new attractive forces* and *five new repulsive forces* come into play. Therefore, repulsive forces predominate and the potential energy of the system increases which leads to unstability. Thus, He_2 represents unstable state and a chemical bond is not formed between helium atoms. Hence, He_2 molecule is not formed.

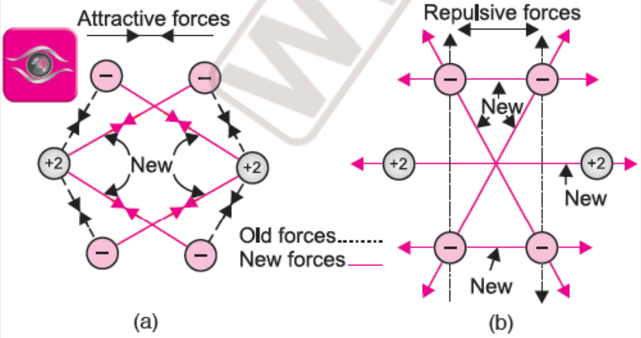


Fig. 23. (*a*) Attractive and (*b*) repulsive forces between helium atoms.

Orbital Overlap Concept of Covalent Bond

When two atoms approach each other, partial merger of two bonding orbitals, known as **overlapping of the orbitals** occurs. The overlapping of orbitals results in the pairing of electrons. The strength of a covalent bond depends upon the extent of overlapping. *The greater the overlapping, the stronger is the bond formed between two atoms.*

Let us explain the formation of a molecule of hydrogen by this method. A hydrogen atom has one electron in 1s-orbital. Now according to Pauli's exclusion principle, an orbital can hold two electrons of opposite spins. When these two atoms having electrons with opposite spins approach each other closely, their orbitals overlap (Fig. 24). Due to the overlapping, the two atomic orbitals merge into a bigger cloud called **molecular orbital.** The molecular orbital contains both the electrons. The two electrons can, therefore, be shared under these conditions. As a result, the two hydrogen atoms are held together in the form of a molecule. Thus, according to orbital theory, the formation of a covalent bond between two atoms results by pairing of electrons with opposite spins belonging to valence shells of two atoms.

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*$1 \text{ pm} = 10^{-12} \text{ m}$, $74 \text{ pm} = 74 \times 10^{-12} \text{ m} = 0.074 \text{ nm} = 0.74$ Å

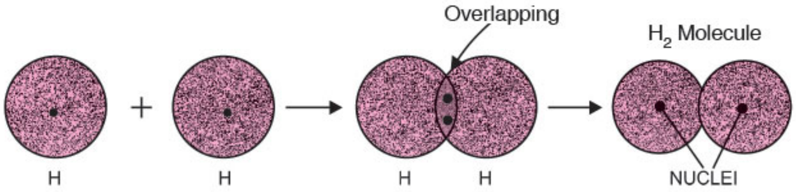


Fig. 24. Overlapping of orbitals of hydrogen atoms.

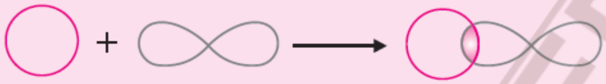
Types of Overlapping and Nature of Covalent Bonds

Depending upon the type of overlapping, the covalent bonds may be divided into two types : (a) *sigma* (σ) *bond* and (b) *Pi* (π) *bond*

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

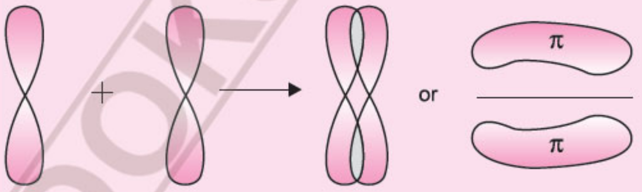
***(i) s-s* overlapping.** In this type, two half-filled *s*-orbitals overlap along the internuclear axis as shown below:

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



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

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



Strength of sigma and *pi*-bonds. The strength of a covalent bond depends upon the extent of overlapping of atomic orbitals forming the bond. During the formation of a sigma bond, the overlapping of orbitals takes place to a larger extent. On the other hand, during the formation of a pi-bond, the overlapping occurs to a smaller extent. Therefore, *a sigma bond is stronger than a pi-bond.*

It is interesting to note that pi-bond between two atoms is formed in addition to a sigma bond. It is always present in the molecules having multiple bonds (double or triple covalent bond).

Comparison of sigma and *pi*-bond. Sigma and *pi*-bonds differ in the following respects :

Table 9. Comparison of sigma and *pi*-bond.

Sigma (σ) Bond	pi(π)Bond
1. A sigma bond is formed by the end to end filled atomic orbitals along the internuclear axis. The overlapping involves two *s*-orbitals, one *s* and *p*-orbital or two *p*-orbitals.	A pi-bond is formed by the sidewise overlap of two half-filled *p*-orbitals.
2. In this case, the overlapping can take place to a larger extent and therefore, the bond formed is a strong bond.	In the formation of π-bond the overlapping occurs to a lesser extent and therefore, the bond is weak.
3. The molecular orbital is symmetrical about the internuclear axis.	The molecular orbital is discontinuous and consists of two charged clouds above and below the plane of atoms.
4. There can be free rotation of atoms around the σ-bond.	Because of overlapping of the electron clouds above and below the plane of the atoms, free rotation of atoms around π-bond is not possible.
5. The bond may be present between two atoms either alone or along with π-bond.	The bond is always present between two atoms in addition to sigma bond.
6. In the formation of sigma bond, *s*-orbitals can participate.	*s*-orbitals cannot participate in the formation of *pi*-bond

DIRECTIONAL PROPERTIES OF COVALENT BONDS

As we have learnt the formation of covalent bond depends largely on the overlap of atomic orbitals between atoms. The formation of a hydrogen (H_2) molecule is essentially due to the overlap of the 1*s* orbitals of two H atoms when they combine with each other. In general, **the greater the extent of overlapping, the stronger is the bond formed.**

In the case of polyatomic molecules like CH_4, NH_3 and H_2O, in addition to formation of bonds, the geometry (shape) of the molecules is also important. For example, why is CH_4 molecule tetrahedral in shape and HCH bond angles are 109°28′. Why is NH_3 molecule pyramidal in shape ?

The valence bond theory explains the formation and the directional properties of bonds in polyatomic molecules in terms of overlap of atomic orbitals and a new concept known as hybridisation of atomic orbitals.

Overlap of Atomic Orbitals

When the two atoms approach each other, their atomic orbitals overlap. The overlap between different types of *s* and *p* orbitals can be positive, negative or zero depending upon the properties of the overlapping atomic orbitals. For example, when two $2p_z$ orbitals overlap along the internuclear axis with the lobes of same sign, then positive overlapping occurs. On the other hand, when these two $2p_z$ orbitals overlap along the internuclear axis with the lobes of opposite sign, negative overlap occurs because lobes of opposite sign cannot combine. Similarly, the different arrangements of *s*- and *p*-orbitals overlap resulting in positive, negative and zero overlaps are shown below :

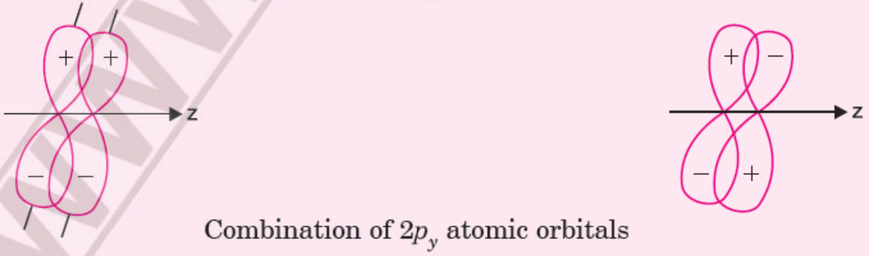
Positive overlap

Negative overlap

Combination of $2p_z$ atomic orbitals

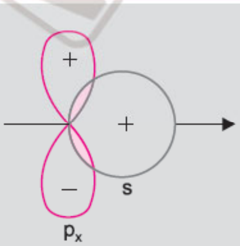
Combination of $2p_z$ and 2*s* atomic orbitals

Combination of $2p_x$ atomic orbitals

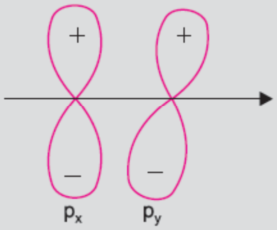


Combination of $2p_y$ atomic orbitals

Zero overlap



Combination of 2*s* and $2p_x$ atomic orbitals



Combination of $2p_x$ and $2p_y$ atomic orbitals

HYBRIDISATION

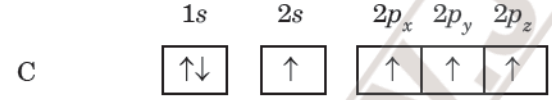
In order to explain the characteristic geometrical shapes of polyatomic molecules, Pauling introduced the concept of hybridisation.

To understand this, let us consider a simple molecule, methane (CH_4). The ground state electronic configuration of carbon is $1s^2\,2s^2\,2p_x^{\,1}\,2p_y^{\,1}\,2p_z^{\,0}$. This may be represented as :

(Ground state)

There are only two half-filled orbitals in the valence shell of carbon. Therefore, its bonding capacity should be two. Carbon is expected to form compounds like CH_2, CCl_2, etc. However, in actual practice, carbon exhibits the bonding capacity of four and is known to form molecules such as CH_4, CCl_4, etc.

This can be explained on the basis of **promotion concept.** In order to explain the bonding capacity of carbon, it was proposed that one of the electrons from 2*s*-filled orbital is promoted to the 2*p*-empty orbital ($2p_z$), which is in a higher energy state. Thus, four half-filled orbitals are formed in valence shell which account for the bonding capacity of four bonds of carbon. This state is known as **excited state** and the process is called **promotion***. Thus, four half filled orbitals get formed in the valence shell which account for the bonding capacity of four of carbon. The electronic configuration of carbon in the excited state is :



(Excited state)

Now the four orbitals of carbon with one unpaired electron can overlap with the 1*s* orbitals of the four H atoms which are also singly filled. This will result in the formation of C–H bonds. However, all the four bonds formed by carbon will not be equivalent. For example, in the formation of CH_4 molecule, one C—H bond will be formed by overlaping of 2*s*- orbital of C and 1*s*- orbital of H whereas the other three C—H bonds will be formed by the overlapping of 2*p*- orbital of C and 1*s*- orbital of H. But in methane (CH_4), all the four bonds of carbon are equivalent. The equivalent character of the bonds can be explained with the help of a new concept known as **hybridisation of atomic orbitals** which was introduced by Pauling. This is an important aspect of Valence Bond Theory.

According to Pauling, the atomic orbitals combine to form new set of equivalent orbitals known as hybrid orbitals. Instead of pure atomic orbitals, these hybrid orbitals are used in bond formation. This process is known as **hybridisation.** This may be defined as :

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

The new orbitals formed as a result of hybridisation are called **hybrid** or **hybridised orbitals**. Thus, to form four equivalent bonds, *one* 2*s* and *three* 2*p*-orbitals of carbon hybridise and form four new orbitals called **sp^3 (pronounced as s–p^3) hybrid orbitals**.

Characteristics of Hybridisation

1. The number of hybridised orbitals formed is equal to the number of the orbitals that get hybridised.
2. The hybridised orbitals are always equivalent in energy and shape.
3. The hybrid orbitals are more effective in forming stable bonds than the pure atomic orbitals.
4. The hybrid orbitals are directed in space in some preferred directions to have stable arrangement. Therefore, the type of hybridisation indicates the **geometry of the molecule.**

Conditions for Hybridisation

(*i*) Only the orbitals present in the valence shell of the atom are hybridised.

(*ii*) The orbitals undergoing hybridisation should have only a small difference in energy. The orbitals which differ largely in energy cannot take part in hybridisation.

(*iii*) Promotion is not essential condition prior to hybridisation.

---

*The promotion of electrons from 2*s* to 2*p* orbital of higher energy level will require an input of energy. From where this energy comes? We know that the formation of covalent bonds is accompained by release of energy. Thus, when reacting atoms say H atoms approach a carbon atom to form covalent bonds, energy is released. This energy released is used to promote one electron from 2*s* to 2*p* orbital.

(*iv*) It is not essential that only half filled orbitals participate in hybridisation. In certain cases, even filled orbitals of valence shell participate in hybridisation.

There are many types of hybridisation involving different atomic orbitals. In the present unit, we shall discuss only the various types of hybridisation involving *s, p* and *d*-orbitals. The different types of hybridisations are discussed below :

1. *sp*-Hybridisation.

In *sp* hybridisation, one *s*- and one *p*-orbitals mix and form two equivalent *sp* hybrid orbitals. The orbitals suitable for *sp* hybridisation are *s* and p_z orbitals, if the hybrid orbitals are to lie along Z–axis. The *sp* hybridisation is pictorially shown below :

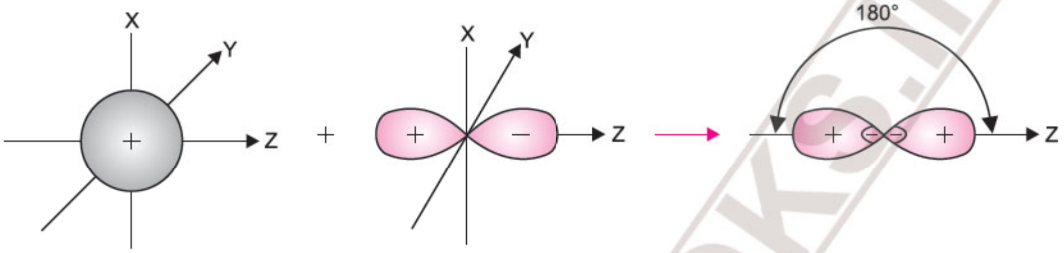


Fig. 25. Formation of *sp* hybrid orbitals.

Each *sp* hybrid orbital has 50% *s*-character and 50% *p*–character. These two *sp* hybrid orbitals point in opposite directions along the Z-axis with bigger positive lobes and very small negative lobes. This provides for more effective overlap resulting in the formation of stronger bonds. These two *sp* hybrid orbitals lie along **linear arrangement** and therefore, it is also called **linear hybridisation.**

The formation of linear molecules like $BeCl_2$, BeF_2, BeH_2 can readily be explained.

Shape of BeF_2 molecule. The electronic configuration of beryllium is $1s^2\,2s^2$. To account for divalency of Be, one of the 2*s*-electrons is promoted to the vacant 2*p*-orbital. These two orbitals (2*s* and 2*p*) get hybridised to form two *sp* hybrid orbitals. These two *sp* hybrid orbitals are oriented in a linear arrangement. Each of these overlaps with 2*p*-orbital of fluorine to form two Be—F bonds. Thus, BeF_2 is **linear** and bond angle is 180°. This is shown below :

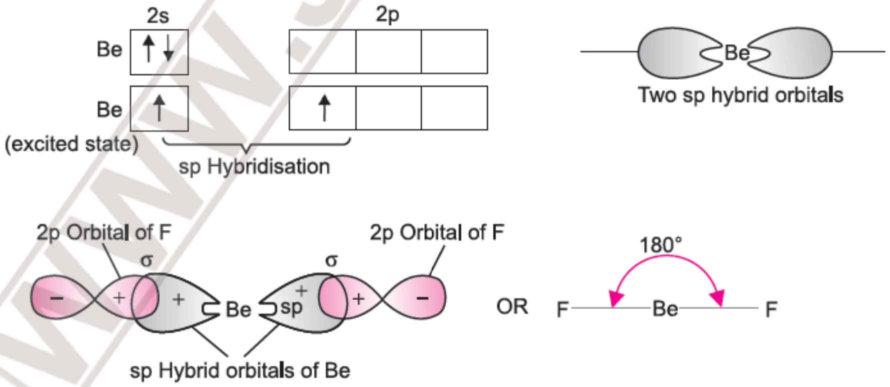


Fig. 26. Formation of BeF_2 molecule.

2. *sp*²-Hybridisation.

In sp^2 hybridisation, one *s* and two *p*-orbitals hybridise to form three equivalent sp^2 hybrid orbitals. Each sp^2 hybrid orbital has one third (33.3%) *s*–character and two-third (66.7%) *p*–character. These three sp^2 hybrids orbitals remain in the same plane making an angle of 120° with one another as shown in Fig. 27. This arrangement is also called **trigonal planar** arrangement and therefore, the molecules involving sp^2 hybridisation of the central atom will adopt **trigonal planar geometry**.

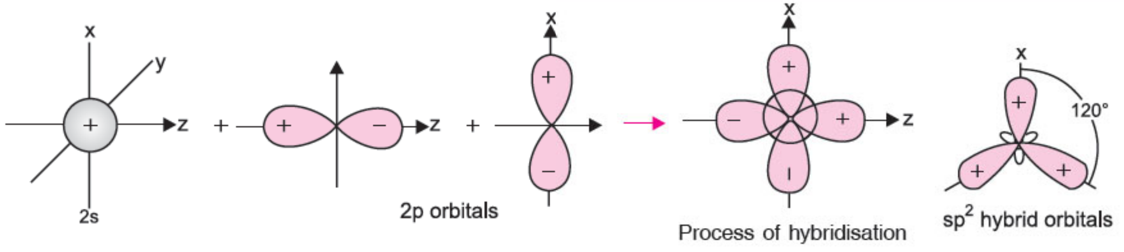


Fig. 27. Formation of three sp^2 hybrid orbitals.

This can be illustrated by considering the example of BCl_3 molecule.

Shape of BCl_3 molecule. In BCl_3, the central boron atom has $1s^2\ 2s^2\ 2p^1$ electronic configuration. To account for trivalency of B, one of the 2s–electrons is promoted to vacant 2p-orbital. Therefore, the excited state of boron has three unpaired electrons. These three orbitals (one 2s and two 2p) hybridise to form three sp^2 hybrid orbitals. These three hybrid orbitals are oriented in a trigonal planar arrangement. Each of these sp^2 hybrid orbitals overlaps with 2p-orbital of chlorine to form three B—Cl bonds. Thus, BCl_3 has **trigonal planar geometry** and ClBCl bond angle is 120°.

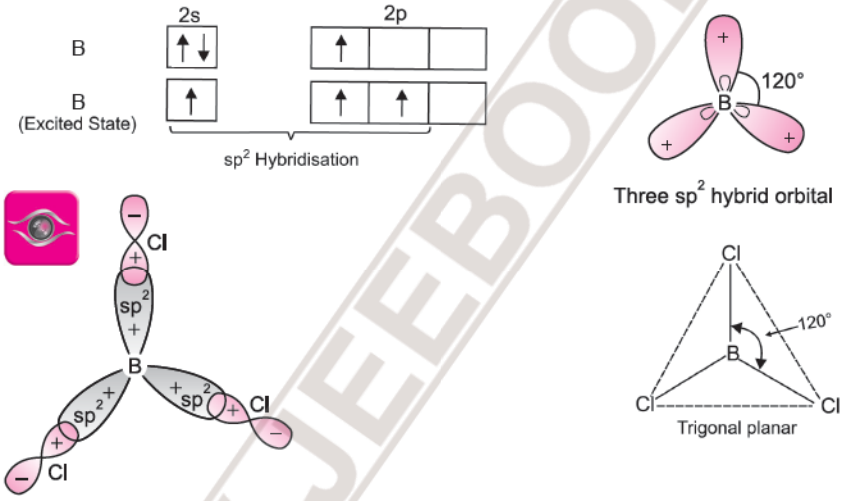


Fig. 28. Formation of BCl_3 molecule.

3. sp^3-Hybridisation.

In sp^3 hybridisation, one s and three p–orbitals hybridise to form four sp^3 hybrid orbitals. The four sp^3

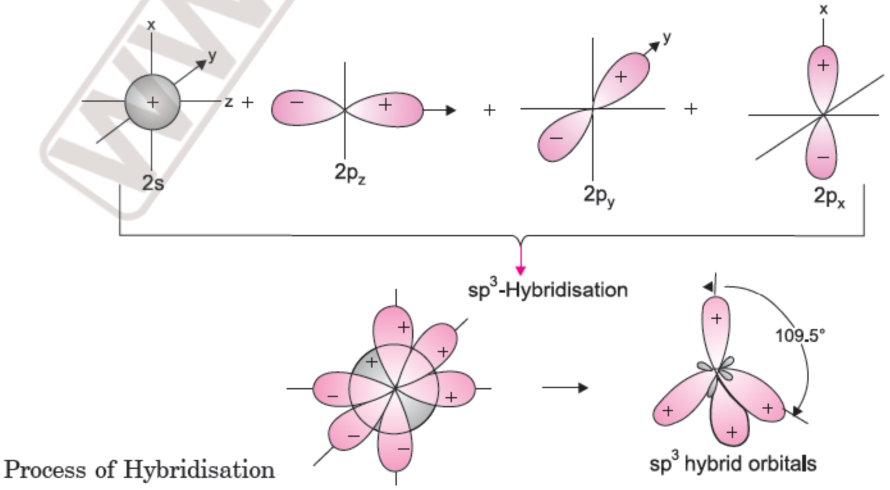


Fig. 29. Formation of four sp^3 hybrid orbitals.

hybrid orbitals will be directed towards the four corners of a regular tetrahedron and make an angle of 109° 28′ (or 109.5°) as shown in Fig. 29. Each sp^3 hybrid orbital has one fourth (25%) s–character and three–fourth (75%) p–character.

This can be illustrated by taking the example of methane (CH_4) molecule.

Formation of methane (CH_4). The central atom carbon has the ground state electronic configuration as $1s^2 2s^2 2p_x^1 2p_y^1$. It has only two unpaired electrons. To account for tetravalency, one of the $2s$–electrons is promoted to vacant $2p$-orbital. Therefore, the excited state of carbon has four unpaired electrons. These four orbitals (one $2s$ and three $2p$) hybridise to form four sp^3 hybrid orbitals, which are oriented in tetrahedral arrangement. Each of these sp^3 hybrid orbital overlaps with $1s$ orbital of hydrogen to form four C – H bonds. Thus, methane molecule has **tetrahedral** geometry with each HCH bond angle of 109.5° as shown in Fig. 30.

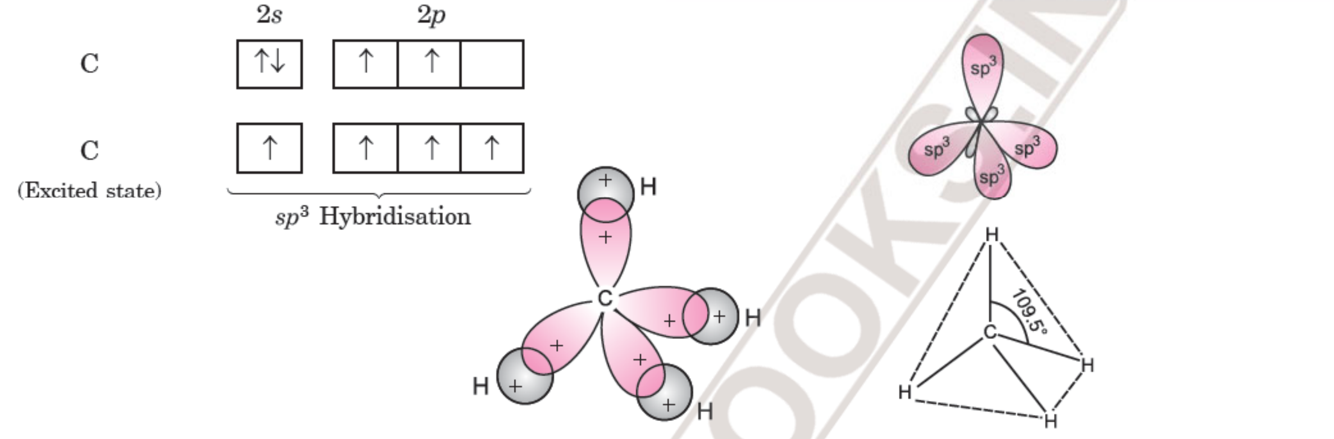


Fig. 30. Formation of CH_4 molecule.

The structures of NH_3 and H_2O can also be explained on the basis of sp^3 hybridisation of N and O bonds in these molecules as explained below :

Ammonia molecule (NH_3). The ground state electronic configuration of nitrogen atom is : $1s^2\,2s^2\,2p_x^{\,1}\,2p_y^{\,1}\,2p_z^{\,1}$. It contains three unpaired electrons in its ground state. Since nitrogen forms only three covalent bonds, there is no need of promotion. These four orbitals ($2s$, $2p_x$, $2p_y$ and $2p_z$) are hybridised to form four sp^3 hybrid orbitals. These four sp^3 hybrid orbitals adopt tetrahedral arrangement. One of these hybrid orbitals contains a lone pair of electrons while the remaining three contain one unpaired electron each. These three hybrid orbitals overlap with $1s$-orbitals of hydrogen atoms to form three N—H sigma bonds.

Thus, in ammonia, the central atom N, is surrounded by three bond pairs (N—H bonds) and one lone pair of electrons.

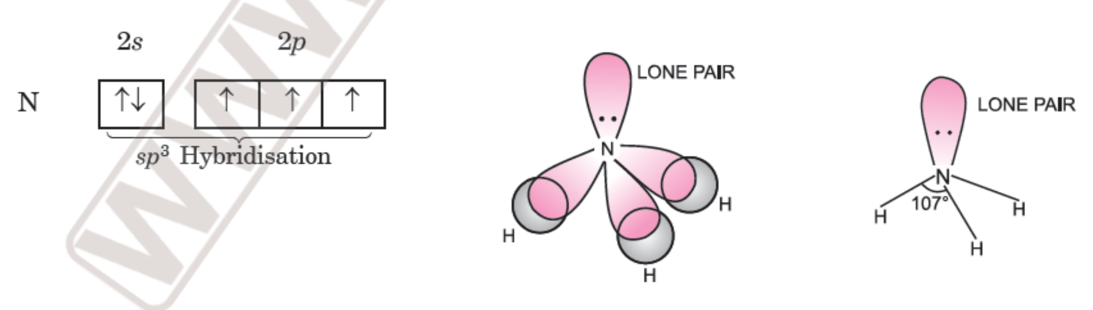


Fig. 31. Formation of ammonia molecule.

We know that the *force of repulsion between a lone pair and a bond pair is greater than the force of repulsion between two bond pairs of electrons*. The molecule, therefore, gets a little distorted and the bond angle H—N—H decreases from 109.5° to 107°. The shape of the molecule is thus **pyramidal** in which the nitrogen atom lies at the centre, three hydrogens form the base and the lone pair of electrons forms the apex of the pyramid.

Water molecule (H_2O). The ground state electronic configuration of the central oxygen atom is : $1s^2\,2s^2\,2p_x^2\,2p_y^1\,2p_z^1$ and is represented in Fig. 32.

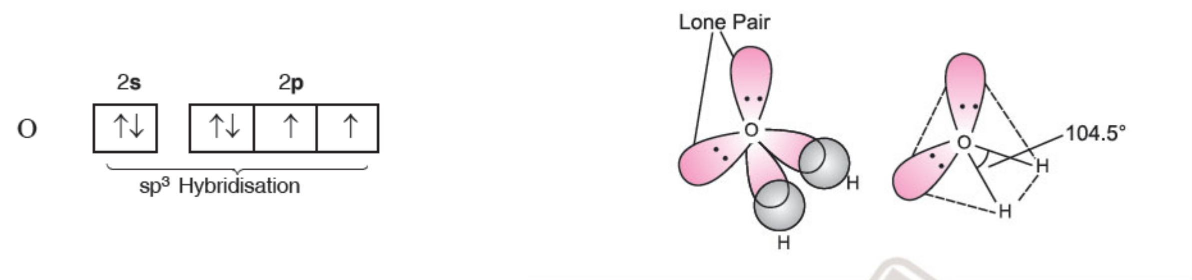


Fig. 32. Formation of water molecule involving sp^3 hybridisation.

Thus, there are two unpaired electrons which can form two bonds with hydrogen atoms, without involving any excitation of the oxygen atom. These four orbitals ($2s$, $2p_x$, $2p_y$ and $2p_z$) *undergo hybridisation to give four sp^3 hybrid orbitals of equivalent energy*. These four sp^3 hybrid orbitals adopt a **tetrahedral structure** with two corners occupied by hydrogen atoms and two corners occupied by lone pairs of electrons as shown in the figure.

Now, we known that the force of repulsion between the two lone pairs of electrons amongst themselves is more than the force of repulsion between a lone pair and a bond pair, which in turn is more than the force of repulsion between two bond pairs of electrons. Therefore, there is greater distortion in this molecule than in ammonia. Consequently, the bond angle HOH in water is even smaller than the bond angle HNH in ammonia. This has been found to be 104.5°. Such a structure is described as **V–shaped** or **angular.**

Unique property of carbon

Carbon has unique property that it can make use of three main types of hybridisations namely sp^3, sp^2 and sp under different conditions. These are discussed below :

1. sp^3 hybridisation of carbon.

As discussed earlier, carbon involves sp^3 hybridisation in methane, CH_4 molecule. Similarly, in ethane C_2H_6, carbon involves sp^3 hybridisation as discussed below :

Formation of ethane. In ethane ($H_3C—CH_3$) molecule, each carbon atom undergoes sp^3 hybridisation. One of the four sp^3 hybrid orbitals of one carbon atom overlaps axially with similar orbital of the other carbon atom to form C—C sigma bond. The remaining three hybrid orbitals belonging to both the carbon atoms overlap axially with the half-filled orbitals of hydrogen atoms to form C—H sigma bonds as shown in Fig. 33.

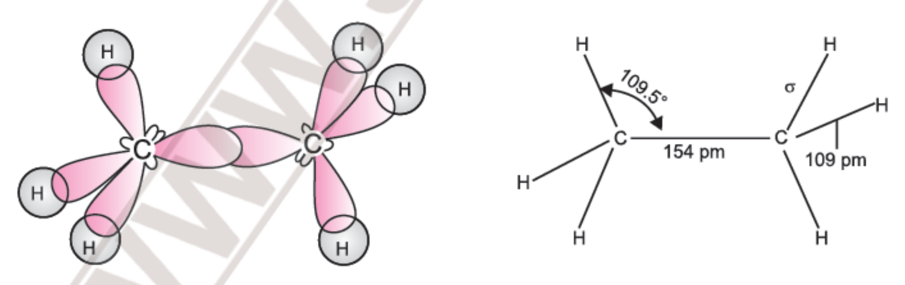


Fig. 33. Orbital picture of ethane.

Thus, in ethane, C—C bond length is 154 *pm* and each C—H bond length is 109 *pm*.

2. sp^2-hybridisation of carbon.

In this type, one s ($2s$) and two p-orbitals ($2p_x$, $2p_y$) present in the valence shell of the excited carbon atom get hybridised to form three equivalent orbitals called **sp^2 hybrid orbitals**.

The orbitals formed are directed towards the three corners of an equilateral triangle with the carbon atom in the centre. The hybridisation is, therefore, known as **trigonal hybridisation**.

Each sp^2 hybrid orbital has one-third s-character and two third p-character. The bond angle between the two hybridised orbitals is 120°. The unhybridised $2p_z$ orbital of carbon is oriented in a plane at right angles to the plane containing three hybridised orbitals as shown dotted in Fig. 34.

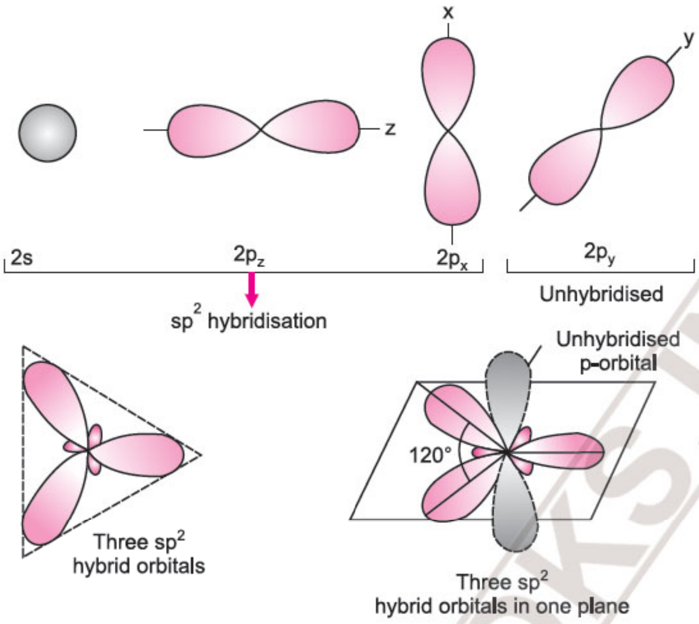
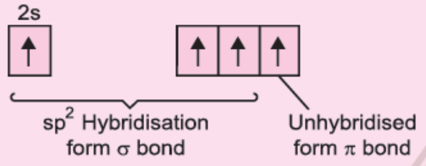


Fig. 34. Representation of sp^2 hybridisation.

Example. Let us illustrate sp^2 hybridisation with the help of ethylene or ethene ($H_2C = CH_2$) molecule.



Carbon atom has four unpaired electrons in the valence shell in the excited state. In the formation of ethylene, each carbon atom undergoes sp^2 hybridisation leaving $2p_z$ orbital unhybridised. One sp^2 hybridised orbital of one carbon atom overlaps axially with sp^2 hybridised orbital of the other carbon atom to form a stable sigma C—C bond. The remaining two sp^2 hybrid orbitals of both carbon atoms overlap axially with the half-filled 1s-orbitals of hydrogen atoms forming four C—H sigma (σ) bonds.

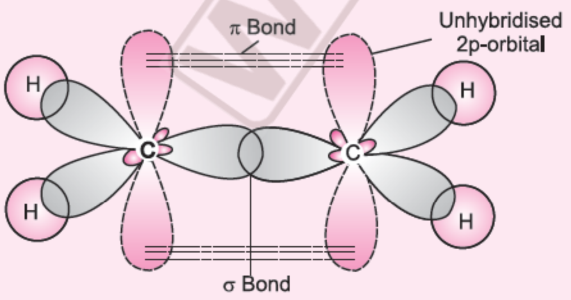


Fig. 35. Orbital picture of ethene.

The unhybridised orbital ($2p_z$) of one carbon atom overlaps sidewise with the similar orbital of the other carbon atom to form weak pi (π) bond. The π-bond consists of two equal electron clouds distributed above and below the plane of other atoms. Thus, in ethylene all the six atoms (forming σ-bonds) lie in one plane and π-bond is at a plane perpendicular to the plane of six atoms (Fig. 36).

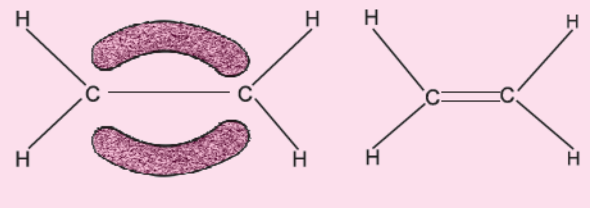


Fig. 36. Electron cloud picture of ethene.

Since there is an equal probability of locating the electron density in both the lobes of the p-orbitals, the same π-bond is formed above and below the internuclear axis representing σ-bond. As pointed out earlier, π-bond is weaker than the σ-bond since the electrons involved are more diffused in space in the molecular form of a cloud. The presence of such a bond in ethene makes it highly reactive in nature. It is, therefore, regarded as *unsaturated* molecule. In ethene molecule,

C=C bond length = 134 pm,
C—H bond length = 108 pm.
H—C—H bond angle = 117.6°,
H—C—C bond angle = 121°.

3. *sp* hybridisation of carbon

In *sp* hybridisation, one *s* (2*s*) and one *p* ($2p_x$) orbitals present in the valence shell of the excited carbon atom get hybridised to form two equivalent orbitals while the remaining two 2*p*-orbitals ($2p_y$ and $2p_z$) do not take part in hybridisation. The entire phenomenon of the electron promotion followed by hybridisation has been shown in Fig. 37. Due to mutual repulsion of the electron clouds, the two hybridised orbitals are inclined to each other at an angle of 180°. The hybridisation is often known as *diagonal hybridisation* and has been represented in Fig. 37. Each *sp* hybrid orbital has equal *s*-and *p*-character, *i.e.*, one-half *s*- and one-half *p*-character.

The two unhybridised orbitals are directed along *y*-axis and *z*-axis while the two hybridised orbitals are directed towards the third axis (*x*-axis).

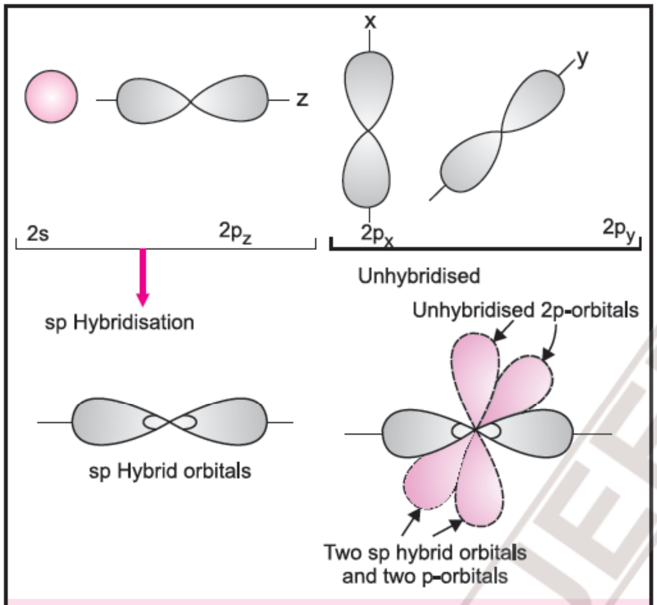


Fig. 37. Representation of *sp* hybridisation.

Example. *sp* type or *diagonal* hybridisation can be illustrated with the help of acetylene or ethyne (HC ≡ CH) molecule.

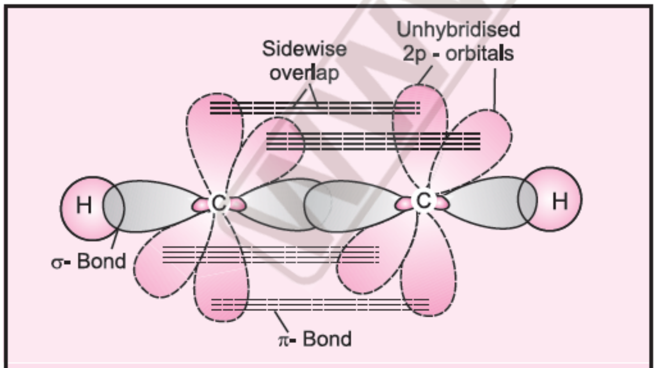
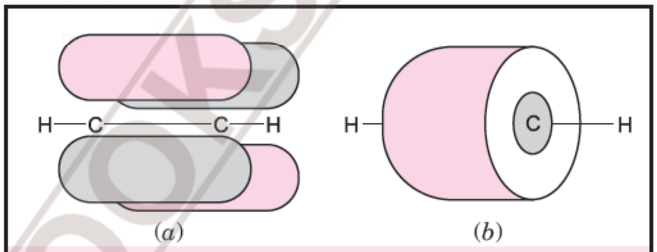


Fig. 38. Orbital picture of ethyne.

In the formation of ethyne, both the carbon atoms undergo *sp*-hybridisation leaving two unhybridised orbitals ($2p_y$ and $2p_z$) on each. One *sp* hybrid orbital of one carbon atom overlaps axially with *sp* hybrid orbital of the other carbon atom to form C—C sigma (σ) bond. The remaining hybridised orbital of each carbon atom overlaps axially with half-filled orbital of hydrogen forming σ-bonds. Each of the two unhybridised orbitals of one carbon atom overlaps sidewise with the similar orbitals of the other carbon atom to form two π-bonds.

So, the triple bond between two carbon atoms is made up of one sigma and two pi bonds. If one π–cloud is pictured as lying above and below the internuclear axis representing σ– bond then the other π-cloud lies in front and in back as shown in Fig. 39 (*a*). However, there is over lapping between the π–cloud so that the four lobes of two π–bonds merge to form a single cylindrical electron cloud about the internuclear axis as shown in Fig. 39. (*b*) Thus in acetylene molecule:

C≡C bond length = 120 pm
C–H bond length = 106 pm
H–C–C bond angle = 180°



(*a*) (*b*)

Fig. 39. Ethyne molecule sharing two π-bonds.

Hybridisation in Elements Involving *d*-orbitals

The elements of third period contain *d*-orbitals also in addition to *s*- and *p*-orbitals. The 3*d*-orbitals are comparable in energy to the 3*s*- and 3*p*-orbitals. These *d*-orbitals are also involved in the hybridisation to explain the geometries of molecules of elements of third period. This results in covalencies of 5, 6 and 7, which are not known amongst the compounds of second period elements. Due to the availability of *d*-orbitals, P and S can exhibit covalency of 5 and 6 respectively whereas the corresponding elements of same group N and O of second period cannot extend their octets.

For example, in the ground state phosphorus and sulphur have three and two half filled orbitals (like nitrogen and oxygen) respectively. Thus, they form compounds like PF_3 and H_2S. But P and S also form hypervalent compounds like PF_5 and SF_6. However, N and O cannot form corresponding SF_6 and OF_6 molecules. This is a **feature of elements of third period** in which they can extend their octets.

Let us understand some common types of hybridisations involving *d*-orbitals and common examples of molecules of third period.

1. sp^3d-hybridisation

This hybridisation involves the mixing of one *s*, three *p* and one *d*-orbitals. These five orbitals hybridise to form five sp^3d-hybrid orbitals. The mixing of five orbitals is shown in Fig. 40. These hybrid orbitals point towards the corners of a *trigonal bipyramidal geometry*. In this case, the three orbitals forming a plane are directed towards the corners of an equilateral triangle while the other two are perpendicular to the plane of the triangle lying above and below it.

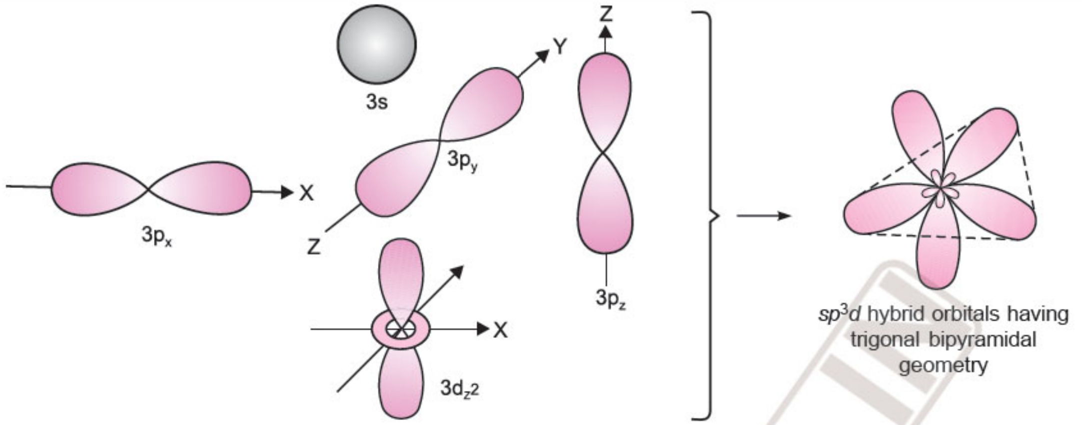


Fig. 40. Formation of five sp^3d hybrid orbitals which adopt trigonal bipyramidal geometry.

Phosphorus pentachloride involves sp^3d hybridisation as described below :

Geometry of PCl_5 molecule. The outer electronic configuration of phosphorus, (Z=15), the central atom, is $3s^2\ 3p^3$ which may be represented as shown in Fig. 41 (*a*). It has three unpaired electrons in the ground state.

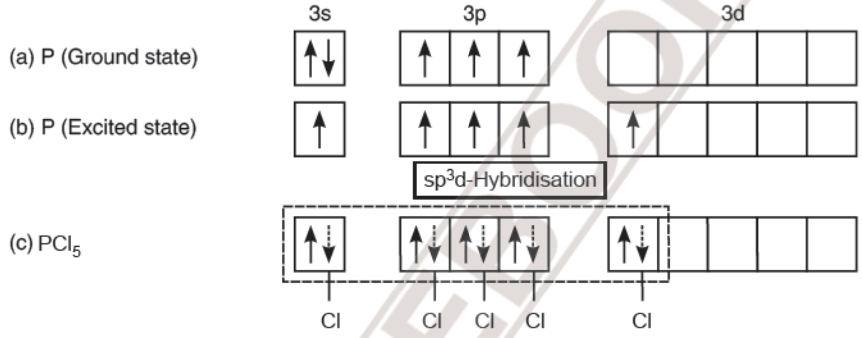


Fig. 41. Formation of PCl_5 molecule involving sp^3d hybridisation.

To explain the pentavalency of phosphorus in PCl_5, one of the electrons in $3s$-orbital is promoted to the higher $3d$-orbital so that it has five unpaired electrons. This is called the excited state of phosphorus and is represented in Fig. 41 (*b*). These five orbitals hybridise to form five sp^3d-hybrid orbitals which adopt trigonal bipyramidal arrangement. Each of the sp^3d-hybrid orbital overlaps with $3p$-orbital of chlorine forming five P—Cl bonds as shown in Fig. 42.

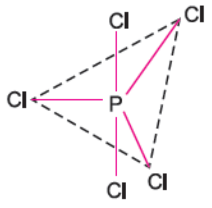


Fig. 42. Structure of PCl_5 molecule.

Thus, PCl_5 molecule has ***trigonal bipyramidal geometry.*** It may be noted that all the bond angles in trigonal bipyramidal geometry are not equivalent. Three bonds lie in one plane at an angle of 120° to one another as in a triangular planar arrangement. These bonds are termed as *equatorial bonds.* Of the remaining two bonds, one lies above and the other below the equatorial plane both making an angle of 90° with the plane. These bonds are called *axial bonds.* It may be remembered that this geometry is not symmetrical. *The axial bonds have been found to be larger than equatorial bonds.* For example, in case of PCl_5 molecule

each P — Cl axial bond = 219 pm

and each P — Cl equatorial bond = 204 pm

The larger bond length of axial bond in comparison to equatorial bond is because of greater repulsion from other bonds in axial position, (already discussed in VSPER theory). Therefore, the axial bonds are slightly larger and hence slightly weaker than equatorial bonds. Therefore, PCl_5 is quite reactive.

PF_5 also have similar hybridisation and geometry.

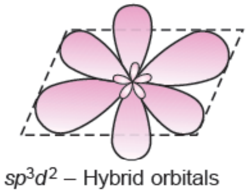


Fig. 43. Six sp^3d^2 hybrid orbitals which adopt octahedral geometry.

2. sp^3d^2-hybridisation.

In this case, one *s*, three *p* and two *d*-orbitals get hybridised to form six sp^3d^2-hybrid orbitals which adopt octahedral arrangement as given in Fig. 43.

Geometry of SF_6 molecule. The geometry of SF_6 molecule can be explained on the basis of sp^3d^2 hybridisation. In SF_6, the central sulphur atom has the ground state configuration, $3s^23p^4$ as shown in Fig. 44. To account for the hexavalency in SF_6, one electron each from 3*s* and $3p_x$ orbitals is promoted to 3*d*-orbitals as shown in Fig. 44 (*a*). These six orbitals get hybridised to form six sp^3d^2-hybrid orbitals. Each of these sp^3d^2-hybrid orbitals overlaps with 2*p*-orbital of fluorine to form S—F bond. Thus, SF_6 molecule has octahedral structure as shown in Fig. 44(*b*). The dotted electrons represent electrons from F-atoms.

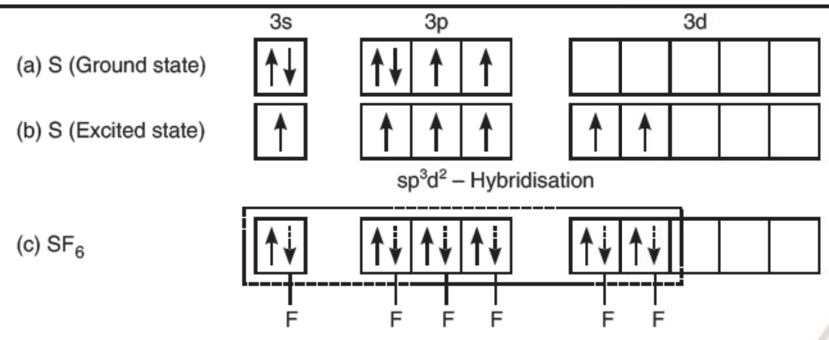


Fig. 44(*a*). Formation of SF_6 molecule involving sp^3d^2-hybridisation

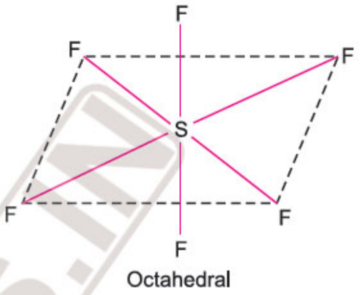


Fig. 44(*b*). Octahedral geometry of SF_6 molecule.

3. sp^3d^3-hybridisation.

This involves the mixing of one *s*, three *p* and three *d*-orbitals forming seven sp^3d^3-hybrid orbitals having **pentagonal bipyramidal geometry.** The geometry of IF_7 molecule can be explained on the basis of sp^3d^3-hybridisation.

Geometry of IF_7 molecule.

The outer electronic configuration of iodine atom is $5s^25p^5$. To make seven bonds, one *s* and two *p*-orbitals are promoted to the higher vacant 5*d*-orbitals as shown in Fig. 45 (*a*) and (*b*). These seven orbitals are then hybridised to give seven sp^3d^3-hybrid orbitals. Each of these sp^3d^3-hybrid orbitals overlaps with 2*p*-orbitals of fluorine to form IF_7 molecule having **pentagonal bipyramidal geometry.**

In this geometry, all the bond angles are not equal. Five F-atoms are directed towards the vertices of a regular pentagon making an angle of 72°. The other two F-atoms are at right angles (90°) to the plane. Due to different bond angles, the bonds are different in length. The axial bonds are larger than equatorial bonds.

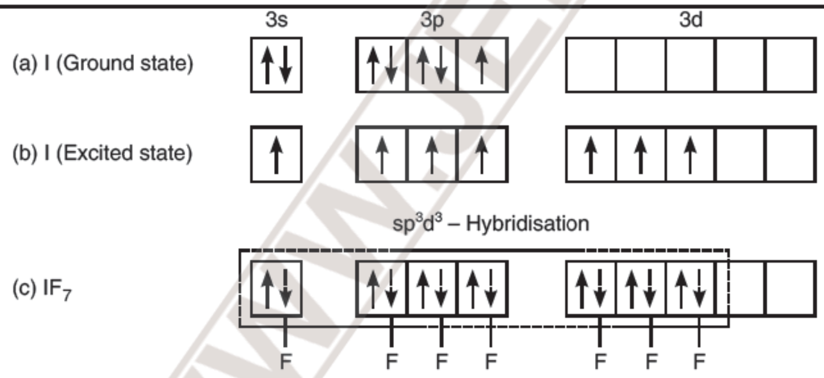
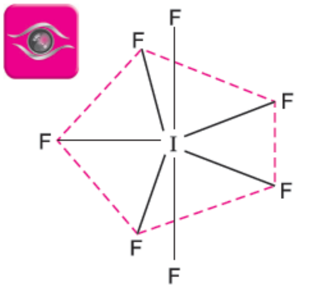


Fig. 45(*a*). Formation of IF_7 molecule involving sp^3d^3-hybridisation

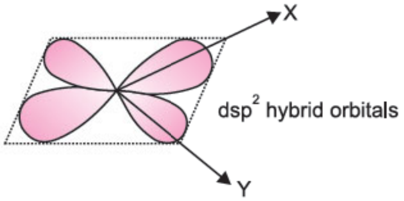


Pentagonal bipyramidal

Fig. 45(*b*). Pentagonal bipyramidal geometry of IF_7 molecule.

4. dsp^2-hybridisation.

In addition to above types of hybridisations, dsp^2 type hybridisation is also known particularly for transition metal ions. The orbitals involved in this type of hybridisation are $d_{x^2-y^2}$, *s* and two *p*. The four orbitals hybridise to give square planar geometry as shown below :



Square planar arrangement

The common example of a molecule involving dsp^2 hybridisation is $[Ni(CN)_4]^{2-}$.

Geometry of $[Ni(CN)_4]^{2-}$ ion. In this case, the oxidation state of nickel is +2. The ground state electronic configuration of nickel is $3d^8 4s^2$. Therefore, the electronic configuration of Ni^{2+} is $3d^8$. When the four CN^- ions come closer to Ni^{2+} ions, the two unpaired d–electrons are paired up thereby making a $3d$–orbital empty. These empty four orbitals (one $3d$, one $4s$ and two $4p$) hybrdise to form four dsp^2 hybrid orbitals. Each one of the four CN^- groups donates a lone pair of electrons to the vacant dsp^2 hybrid orbitals as shown

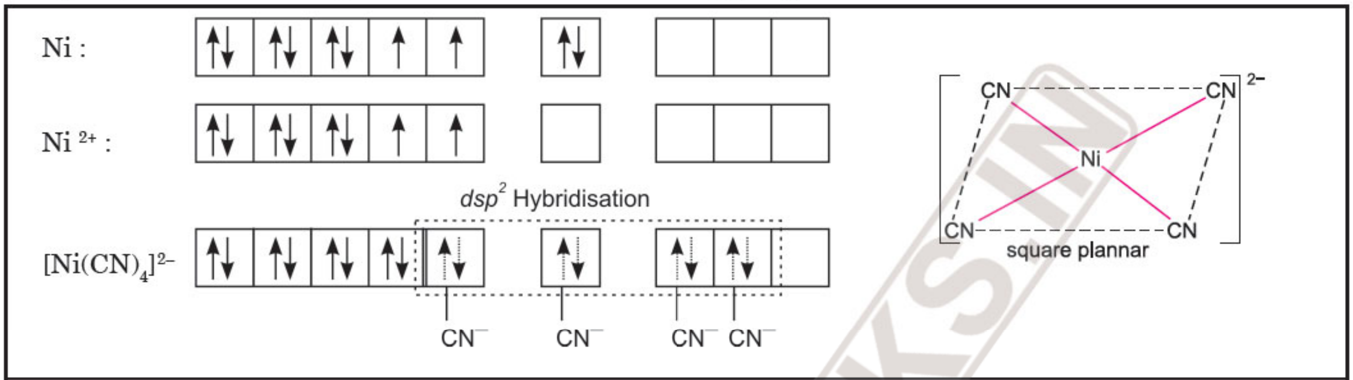


Fig. 46. Formation of $[Ni(CN)_4]^{2-}$ involving dsp^2 hybridisation of nickel. The dotted electrons are supplied by CN^- ions.

Thus, $[Ni(CN)_4]^{2-}$ has square planar geometry. It may be noted that in this case, the vacant orbitals are hybridised. The CN^- groups donate pair of electrons in these hybridised vacant orbitals.

REMEMBER

The d-orbitals used in different types of hybridisations

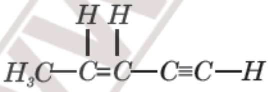
- sp^3d : d_{z^2}
- sp^3d^2 : $d_{x^2-y^2}, d_{z^2}$
- sp^3d^3 : d_{xy}, d_{yz}, d_{zx}
- dsp^2 : $d_{x^2-y^2}$

SOLVED EXAMPLES

Example 12.

What is the total number of sigma and pi bond in the following molecules :

(i) CH_2Cl_2 *(ii)*

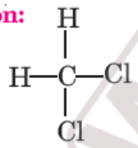


$H_3C-\overset{H}{C}=\overset{H}{C}-C\equiv C-H$

(iii) C_2H_3Cl

Solution:

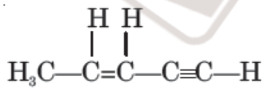
(i)



$H-\underset{Cl}{\overset{H}{C}}-Cl$

No. of σ bonds = 4
No. of π bonds = 0

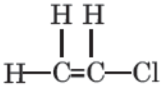
(ii)



$H_3C-\overset{H}{C}=\overset{H}{C}-C\equiv C-H$

No. of σ bonds = 10
No. of π bonds = 3

(iii)



$H-\overset{H}{C}=\overset{H}{C}-Cl$

No. of σ bonds = 5
No. of π bonds = 1

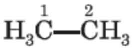
Example 13.

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

(i) H_3C-CH_3 *(ii)* $H_3C-CH=CH_2$
(iii) CH_3CHO *(iv)* CH_3COOH
(v) CH_3-CH_2-OH **N.C.E.R.T.**

Solution:

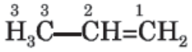
(i)



$H_3\overset{1}{C}-\overset{2}{C}H_3$

C–1 and C–2 : sp^3 hybridised,

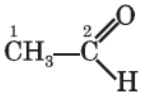
(ii)



$\overset{3}{H_3}\overset{3}{C}-\overset{2}{C}H=\overset{1}{C}H_2$

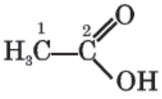
C–1 : sp^2 hybridised,
C–2 : sp^2 hybridised,
C–3 : sp^3 hybridised

(iii)



C–1 : sp^3 hybridised,
C–2 : sp^2 hybridised

(iv)



C–1 : sp^3 hybridised,
C–2 : sp^2 hybridised,

(v)

$\overset{2}{C}H_3-\overset{1}{C}H_2-OH$

C–1 : sp^3 hybridised
C–2 : sp^3 hybridised

Example 14.

Is there any changes in the hybridisation of B and N atoms as a result of the following reaction :

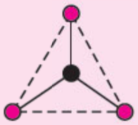
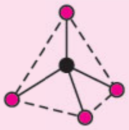
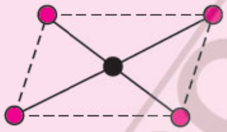
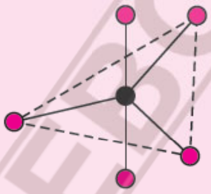
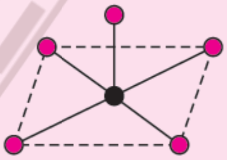
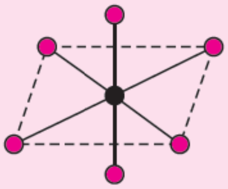
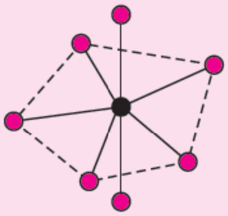
$BF_3 + NH_3 \longrightarrow F_3B-NH_3$? **N.C.E.R.T.**

Solution: In BF_3, the hybridisation of B is sp^2 and in NH_3 , the hybridisation of N is sp^3.

After the reaction, the hybridisation of B changes to sp^3 but the hybridisation of N remains unchanged (sp^3).

The hybridisation and molecular shapes of some molecules are summarised in Table 10.

Table 10. Hybrid orbitals and molecular shapes of molecules involving *d*-orbitals

Type of hybridisation	Atomic orbitals	Shape	Bond angle	Examples
sp	$s + p$	 Linear	180°	BeH_2, $HgCl_2$ $BeCl_2$, $ZnCl_2$, C_2H_2
sp^2	$s + 2(p)$	 Trigonal planar	120°	BF_3, BCl_3, $AlCl_3$, C_2H_4, CO_3^{2-}, NO_3^-
sp^3	$s + 3(p)$	 Tetrahedral	109.5°	CH_4, $SnCl_4$, $SiCl_4$, SiF_4, NH_4^+, ClO_4^-
dsp^2 (d is $d_{x^2-y^2}$)	$d + s + 2(p)$	 Square planar	90°	$[Ni(CN)_4]^{2-}$, $[Pt\ Cl_4]^{2-}$
sp^3d (d is d_{z^2})	$s + 3\ (p) + d$	 Trigonal bipyramidal	90°, 120°	PF_5, PCl_5
dsp^3 (d is d_{z^2})	$d + s + 3(p)$	 Square pyramidal	90°	BrF_5, $XeOF_4$
sp^3d^2 or d^2sp^3 (d are $d_{x^2-y^2}$, d_{z^2})	$s + 3\ (p) + 2\ (d)$ or $2(d) + s + 3(p)$	 Octahedral	90°	SF_6, CrF_6^{3-} $[Co(NH_3)_6]^{3+}$
sp^3d^3 (d are d_{xy}, d_{yz}, d_{zx})	$s + 3(p) + 3(d)$	 Pentagonal bipyramidal	90° 72°	IF_7

add on Conceptual Questions 2

Q. 1. Out of σ and π bonds, which one is stronger bond and why ?

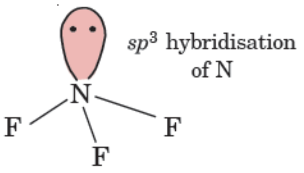
Ans. σ bond is stronger than a π bond. This is because σ-bond is formed by head on overlapping of orbitals and therefore, overlapping is large. On the other hand, π-bond is formed by the sidewise overlapping, which is small.

Q. 2. Which of the following molecules will have zero dipole moment : $SiCl_4$, H_2O, CO_2, BF_3, NH_3 ?

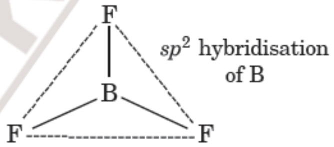
Ans. $SiCl_4$, CO_2 and BF_3 will have zero dipole moment.

Q. 3. Why NF_3 is pyramidal while BF_3 is triangular planar, though both are tetra atomic molecules?

Ans. In NF_3, nitrogen involves sp^3 hybridisation and one position is occupied by a lone pair. Therefore, the molecule is pyramidal. But in BF_3, B involves sp^2 hybridisation having triangular planar geometry.



Pyramidal



Triangular planar

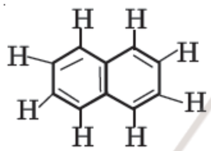
Q. 4. Which of the following has larger bond angle in each pair ?

(*i*) CO_2, BF_3 (*ii*) NH_3, CH_4 (*iii*) H_2O, H_2S (*iv*) SiF_4, C_2H_2

Ans. (*i*) CO_2 (*ii*) CH_4 (*iii*) H_2O (*iv*) C_2H_2

Q. 5. How many σ and π bonds are present in naphthalene ?

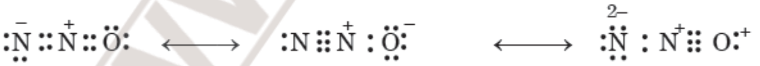
Ans. Naphthalene is



σ bonds = 19, π bonds = 5

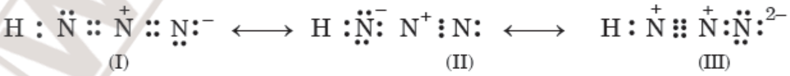
Q. 6. Draw resonating structures of (*i*) nitrous oxide (N_2O) and (*ii*) hydrazoic acid (HN_3) molecule.

Ans. (*i*) Nitrous oxide, N_2O



In this, structure III is unfavourable because it has positive charge on the electronegative oxygen atom and also has electric charges of same sign on the adjacent atoms.

(*ii*) Hydrazoic acid, HN_3



Structure III is unfavourable because of positive charges on adjacent N-atoms and double negative charge on the third N-atom.

Q. 7. Arrange H_2O, NH_3 and CH_4 in the decreasing order of bond angle.

Ans. Bond angle decreases as :

$$CH_4 > NH_3 > H_2O$$

Q. 8. Benzene ring has alternate single and double bonds, yet all the C–C bonds are of equal lengths. Why ?

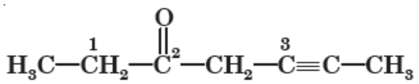
Ans. Due to resonance in benzene, all carbon-carbon bonds have same bond lengths (between single and double).

Q. 9. Arrange the following bonds in order of increasing polarity :

P—H, H—O, C—Cl

Ans. Order of polarity is : P—H < C—Cl < H—O

Q. 10. **Arrange the following carbon atoms numbered C–1, C–2 and C–3 in the decreasing order of *s*-character :**



$$H_3C-\overset{1}{C}H_2-\overset{\overset{O}{\|}}{C^2}-CH_2-\overset{3}{C}\equiv C-CH_3$$

Ans. Decreasing order of *s*-character

C – 3 > C – 2 > C – 1

Q. 11. **Select the molecule or ion having larger property mentioned in each of the following pairs :**

(*a*) **NF_3, NH_3 : dipole moment**

(*b*) **NH_3, PH_3 : bond angle**

(*c*) **CO_2, BF_3 : bond angle**

Ans. (*a*) NH_3 (*b*) NH_3 (*c*) CO_2

Q. 12. **What type of hybridisation is involved in carbon atoms of benzene ?**

Ans. sp^2

Q. 13. **Indicate whether the following statement is TRUE or FALSE. Justify your answer in not more than three lines.**

The dipole moment of CH_3F is greater than that of CH_3Cl.

Ans. **True**. This is because C–F bond is more polar than C–Cl bond due to larger electronegativity of F than Cl. As a result, the resultant dipole moment of CH_3F is more.

Q. 14. **Which of the following has maximum bond angle ?**

H_2O, CO_2, NH_3, CH_4

Ans. CO_2 due to its linear structure.

Q. 15. **CO_2 is non-polar while H_2O is polar. What conclusion do you draw about their structures from these ?**

Ans. CO_2 is a linear molecule, therefore the resultant dipole moment of two C = O bonds get cancelled giving zero dipole moment. On the other hand, water molecule is not linear. It has angular shape and the bond moments of two O–H bonds give resultant dipole moment.

Q. 16. **Select the correct choice (no reasons)**

(a) Which of the two is more hard : MgO or CaO ?

(b) Which of the two has more ionic character : HCl or HBr ?

Ans. (*a*) MgO, (*b*) HCl

Q. 17. **Arrange the following bonds in the order of increasing ionic character :** ***N.C.E.R.T.***

C – H, F – H, Br – H, Na – I, K – F and Li – Cl

Ans. C – H < Br – H < F – H < Li – Cl < Na – I < K – F.

Q. 18. **Arrange the following molecules in order of increasing ionic character of their bonds :**

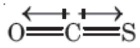
LiF, K_2O, N_2, SO_2, ClF_3 ***N.C.E.R.T.***

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

Q. 19. **Which of the two molecules OCS and CS_2 has a higher dipole moment and why ?** ***N.C.E.R.T.***

Ans Both OCS and CS_2 are linear molecules having, Lewis structure as :

and

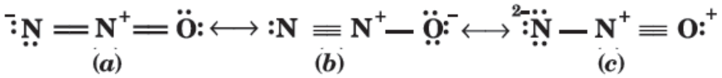


In CS_2, the dipole moment is 0 because the bond moments cancel out. But in OCS, bond moment of C = O is not equal to that of C = S. Hence, it has a net dipole moment. Thus, dipole moment of OCS is higher.

Q. 20. **Which type of hybridisation explain the trigonal bipyramidal shape of SF_4 ?**

Ans. sp^3d hybridisation.

Q. 21. **Nitrous oxide (N_2O) may be represented by the following structures**



Which of these contributes least ?

Ans. Structure (*c*) contributes the least because it has positive charge on oxygen atom and has electric charges of same sign on the adjacent atoms.

MOLECULAR ORBITAL THEORY

Molecular orbital theory was developed by F. Hund and R.S. Mulliken in 1932. The basic idea of molecular orbital theory is that atomic orbitals of individual atoms combine to form molecular orbitals. The electrons in molecules are present in the molecular orbitals which are associated with several nuclei. These molecular orbitals are filled in the same way as the atomic orbitals in atoms are filled.

Salient Features of Molecular Orbital Theory

The salient features of the molecular orbital theory are :

1. Just like an atom, molecule has orbitals of definite energy levels. Like electrons of atoms are present in atomic orbitals, electrons of a molecule are present in different molecular orbitals.

2. Molecular orbitals are formed by the combination of atomic orbitals of proper symmetry and comparable energies. The atomic orbitals of these atoms merge into molecular orbitals.

3. An electron in an atomic orbital is under the influence of only one nucleus. However, an electron in a molecular orbital is under the influence of two or more nuclei depending upon the number of atoms present in the molecule.

Thus, an atomic orbital is monocentric while a molecular orbital is polycentric.

4. Just as the electron probability distribution around a nucleus in an atom is given by an atomic orbital, the electron probability distribution around a group of nuclei in a molecule is given by molecular orbital.

5. ***The number of molecular orbitals formed is equal to the number of combining atomic orbitals***. When two atomic orbitals combine, they form two molecular orbitals. These are called ***bonding molecular orbital*** and ***antibonding molecular orbital***.

6. The bonding MO has lower energy and hence greater stability whereas corresponding antibonding MO has more energy and hence lesser stability.

7. The molecular orbitals are filled in same way as atomic orbitals are filled in accordance with Aufbau principle, Pauli exclusion principle and Hund's rule.

Molecular orbitals are formed by the combination of atomic orbitals of bonded atoms. We have learnt that according to wave mechanics, the atomic orbitals can be expressed by wave functions (ψ's). The wave functions represent the amplitude of the electron waves. These are obtained from the solutions of Schrodinger wave equation. Similarly, we can write Schrodinger wave equation for the whole molecule. However, it is very difficult to solve the wave equation for molecules. To overcome this problem, scientists have used an approximate method known as **linear combination of atomic orbitals abbreviated as LCAO method.**

Formation of Molecular orbitals

According to LCAO method, the orbitals are formed by the linear combination (addition or subtraction) of atomic orbitals of the atoms which form the molecule. Let us apply this theory to hydrogen molecule. Consider that hydrogen molecule consists of two atoms A and B. Each of these atoms has 1*s*-orbital of lowest energy. The atomic orbitals of these atoms may be represented by the wave functions ψ_A and ψ_B for hydrogen atoms A and B respectively. Now, when these atomic orbitals are brought closer, they combine to form molecular orbitals. According to LCAO method, the linear combination of atomic orbitals can take place by addition and by subtraction of wave functions of atomic orbitals.

i.e., $\psi_{MO} = \psi_A \pm \psi_B$

These two types of combinations give rise to two molecular orbitals as described below :

(*i*) Molecular orbital obtained by **addition of wave functions** of atoms may be represented as :

$$\psi(MO) = \psi_A + \psi_B$$

or $\quad \sigma = \psi_A + \psi_B$

This molecular orbital is called **bonding molecular orbital.**

(*ii*) Molecular orbital obtained by **subtraction of wave functions** of atoms may be represented as :

$$\psi^*(MO) = \psi_A - \psi_B$$

or $\quad \sigma^* = \psi_A - \psi_B$

The molecular orbital is called **antibonding molecular orbital.**

The physical picture of bonding and antibonding molecular orbitals can be obtained by considering the atomic orbitals. To illustrate this, we may take the combination of 1*s*-orbital of one hydrogen atom with 1*s*-orbital of second hydrogen atom to form two molecular orbitals in hydrogen molecule. As discussed above, there are two ways of combining atomic orbitals. The molecular orbital formed by the addition of overlapping of two 1*s*-orbitals is shown in Fig. 47. It is clear from the figure that the region between the two nuclei where the two 1*s*-atomic orbitals overlap has high electron density. Therefore, repulsion between the nuclei is very less. Such a molecular orbital is called **bonding molecular orbital.** It is designated as σ 1*s* (called sigma 1*s*) orbital. The sigma (σ) signifies that the orbital is symmetrical about the molecular axis and the script '1*s*' indicates that it is formed by the combination of 1*s*-atomic orbitals.

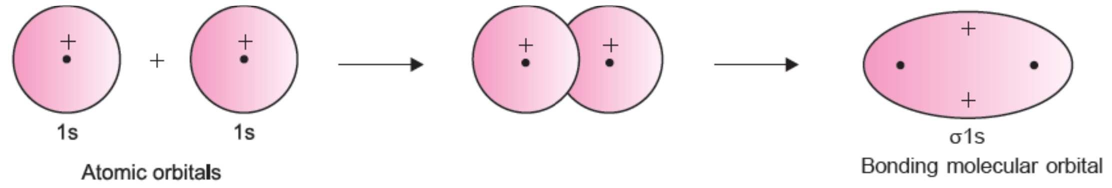


Fig. 47. Formation of bonding molecular orbital.

The molecular orbital formed by the subtraction of overlapping of two 1*s*-orbitals is shown in Fig. 48.

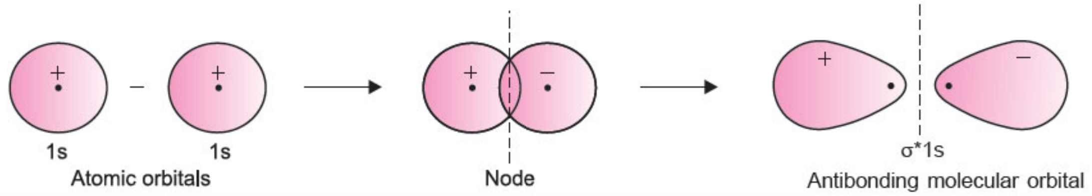


Fig. 48. Formation of antibonding molecular orbital.

It is clear from the figure that the electron density in between the two nuclei is practically zero and most of the electron density is located away from the space between the two nuclei. This is because, the electron probability densities of two atomic orbitals get cancelled in the centre (by subtraction) so that there is no probability of finding the electron in the region of overlap *i.e.* between the nuclei. In fact, there is a nodal plane (on which the electron density is zero) between the nuclei and hence the repulsion between the nuclei is high. This situation does not favour the bond formation. Such an orbital is called **anti-bonding molecular orbital.** It is designated as σ*1*s* (called sigma star 1*s*). The asterisk '*' is used to represent antibonding molecular orbital.

Thus, **the bonding molecular orbital is designated as σ 1*s* (called sigma bonding) and antibonding molecular orbital is designated as σ* 1*s* (called sigma antibonding).**

Differences between atomic and molecular orbitals

The important differences between atomic and molecular orbitals are :

Atomic orbital	Molecular orbital
1. An electron in atomic orbital is under the influence of only one positive nucleus of the atom.	An electron in molecular orbital is under the influence of two or more nuclei depending upon the number of atoms present in the molecule.
2. Atomic orbitals are inherent property of an atom.	Molecular orbitals are formed by the combination of atomic orbitals.
3. They have simple shapes.	They have complex shapes.

The formation of bonding and antibonding molecular orbitals can be explained in terms of *constructive interference (or additive effect) and destructive interference (or subtractive effect)* of the electron waves of the combining atoms.

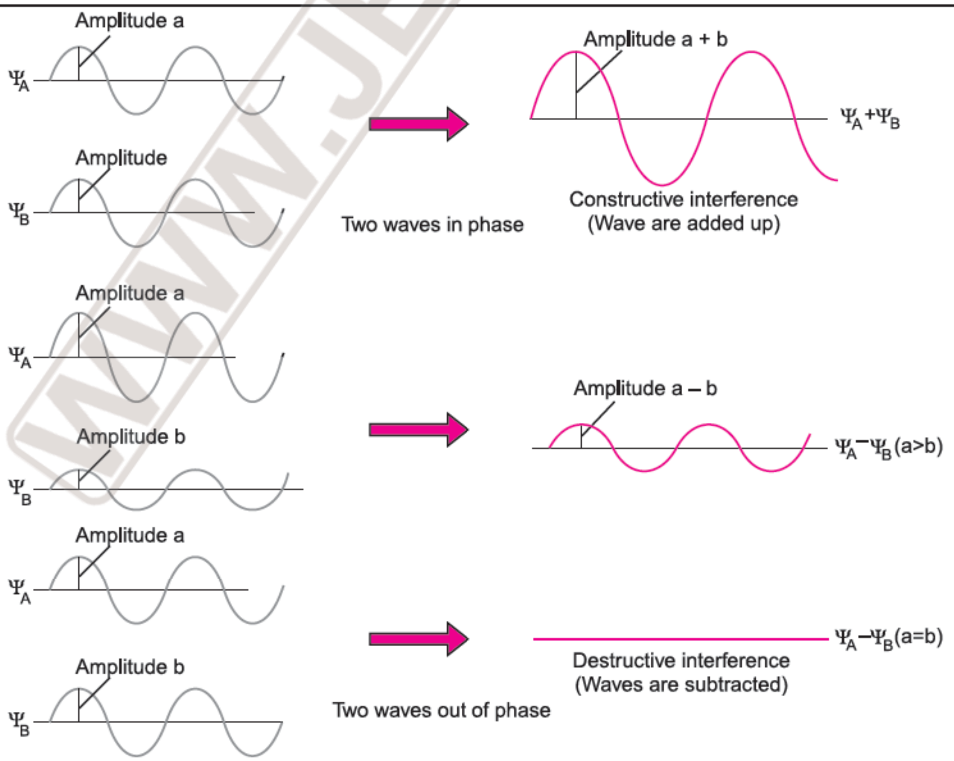


Fig. 49. Constructive and destructive interference of waves.

(*i*) **During constructive interference**, *the two waves are in phase* and the amplitudes of the waves get *added up*. Therefore, the resulting wave function has more electron density in between the nuclei. This corresponds to bonding MO.

(*ii*) On the other hand, when the *two waves are out of phase,* there is **destructive interference** and the amplitudes of the waves get *subtracted* or *cancelled*. Therefore, the resulting wave function has less electron density between the nuclei. This also gives rise *to nodal plane between two nuclei.* This corresponds to wave function of antibonding MO.

The probability density in bonding and antibonding MOs can also be shown by simple mathematics. We know that the probability density is given by square of wave function (ψ^2).

For bonding MO,

$$\psi = \psi_A + \psi_B, \quad \text{so that}$$
$$\psi^2 = (\psi_A + \psi_B)^2 = \psi_A^2 + \psi_B^2 + \mathbf{2\psi_A \psi_B}$$

Thus, ψ^2 is greater than $\psi_A^2 + \psi_B^2$ (sum of the probability densities of individual atoms) by an amount equal to $2\psi_A \psi_B$. Therefore, *the probability of finding electrons in the bonding MO is greater than in either of atomic orbitals* (ψ_A or ψ_B).

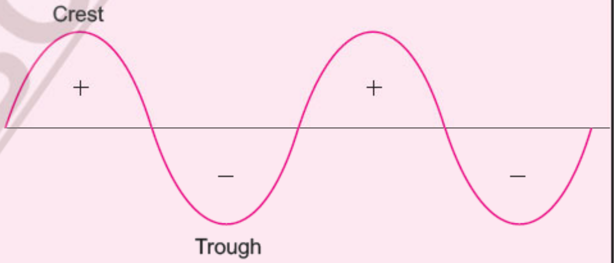
For antibonding MO,

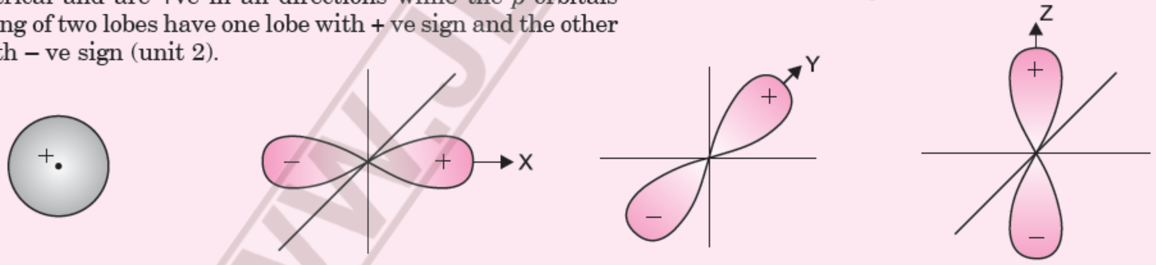
$$\psi^* = \psi_A - \psi_B, \text{ so that}$$
$$\psi^{*2} = (\psi_A - \psi_B)^2 = \psi_A^2 + \psi_B^2 - \mathbf{2\psi_A \psi_B}$$

Thus, ψ^{*2} is less than $\psi_A^2 + \psi_B^2$ by an amount equal to $2\psi_A \psi_B$. Therefore, *the probability of finding the electrons in antibonding MO is less than that in either of the atomic orbitals* (ψ_A or ψ_B).

Note. The positive signs in the *s*-orbitals in Figs. 47 and 48 correspond to the signs of the wave function ψ's. The wave function may have + or – signs.

These signs correspond to + and – signs of the waves. It may be noted that crests of the electron wave are usually given '+' sign and the troughs are given '–' sign. The bonding MO is obtained by the combination of '+' with '+' or '–' with '–' part of the electron wave. On the other hand, antibonding MO is obtained by the combination of '+' with '–' part. To understand the overlapping of two bonding orbitals, it is necessary to give + or – signs of wave functions. It may be remembered that *s*-orbitals are spherically symmetrical and are +ve in all directions while the *p*-orbitals consisting of two lobes have one lobe with + ve sign and the other lobe with – ve sign (unit 2).





s-Orbital 2p$_x$-Orbital **Fig. 50.** 2p$_y$-Orbital 2p$_z$-Orbital

During overlapping or combination of atomic orbitals, only + + or – – lobes can combine. No combination is possible between + and – lobes.

It must be remembered that these '+' and '–' signs have nothing to do with the electrical charges on the orbitals.

RELATIVE ENERGIES OF BONDING AND ANTIBONDING MOLECULAR ORBITALS

We have learnt that in the case of bonding molecular orbital, the attraction of both the nuclei for both the electrons is increased. This results in lowering of energy. In the case of antibonding molecular orbital, the electrons try to go away from the nuclei and this corresponds to repulsive state. The energy of this orbital will be higher. The relative energies of bonding and antibonding molecular orbitals along with atomic orbitals can be represented as shown in Fig. 51.

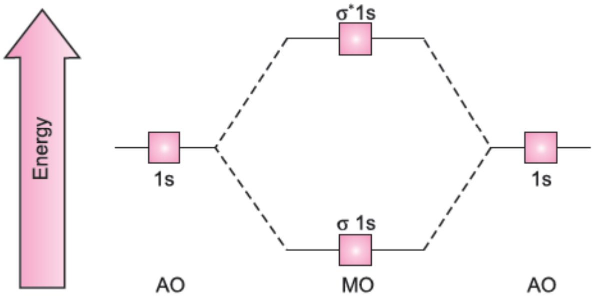


Fig. 51. Relative energies of σ 1*s* and σ*1*s* molecular orbitals.

Thus, the *bonding* molecular orbital is *stabilized* relative to the energy of the isolated atoms and *anti-bonding* molecular orbital is *destabilized* relative to the individual atoms. Further, it may be noted that *the bonding MO is stabilized to the same extent as the antibonding MO is destabilized.*

Differences between Bonding and Anti-bonding Molecular Orbitals

Bonding MO	Anti-bonding MO
1. Bonding molecular orbital is formed by the addition of overlapping of atomic orbitals. The wave function of the bonding MO may be written as : $\psi(\mathrm{MO}) = \psi_A + \psi_B$	Anti-bonding molecular orbital is formed by the subtraction of overlapping of atomic orbitals. The wave function for the ant-bonding MO may be written as : $\psi^*(\mathrm{MO}) = \psi_A - \psi_B$
2. They are formed when the lobes of the combining atomic orbitals have same sign.	They are formed when the lobes of the combining atomic orbitals have opposite sign.
3. It has greater electron density in the region between the two nuclei of bonded atoms.	It has lesser electron density in the region between the two nuclei of the atoms.
4. The forces in this orbital tend to bring the two nuclei of the atoms together. Therefore, the electrons in the bonding MO contribute to attraction between the two atoms.	The forces in this orbital push the nuclei apart. Therefore, the electrons in antibonding MO contribute to repulsion between the atoms.
5. It possesses lower energy than the isolated atomic orbitals.	It possesses higher energy than the isolated atomic orbitals.

COMBINATION OF 2*s* AND 2*p* ATOMIC ORBITALS TO FORM MOLECULAR ORBITALS

Combination of 2*s* atomic orbitals

Like 1*s*-orbitals, 2*s*-orbitals combine by addition and subtraction of overlapping to form bonding and antibonding molecular orbitals. These are labelled as $\sigma 2s$ and $\sigma^* 2s$. These molecular orbitals have exactly the same shapes as $\sigma 1s$ and $\sigma^* 1s$ MOs but they are slightly larger in size.

Combination of 2*p* atomic orbitals

There are three *p*-orbitals namely $2p_x$, $2p_y$ and $2p_z$ which are directed in space along the *x*, *y* and *z* coordinate axes respectively. By convention, ***we can assume z-axis as the internuclear axis.*** The *x* and *y*-axes would then be perpendicular to the internuclear axis. The combination of 2*p*-orbitals forms two types of MOs; sigma (σ) MOs and pi (π) MOs as discussed below :

***(i)* Formation of σ-molecular orbitals.** When the two $2p_z$ orbitals are brought closer along the internuclear axis, they overlap head on forming σ-bond (Fig. 52). When the two orbitals overlap by the addition of electron waves (*i.e.,* with proper signs, ++ lobes overlap), bonding molecular orbital is formed. This may be designated as $\sigma 2p_z$. On the other hand, when the two wave functions are subtracted, an antibonding molecular orbital is formed. This is designated as $\sigma^* 2p_z$. Thus, two $2p_z$ atomic orbitals combine to form two molecular orbitals, *i.e.* a bonding M.O. ($\sigma 2p_z$) and an antibonding M.O. ($\sigma^* 2p_z$).

***(ii)* Formation of π-molecular orbitals.** When a $2p_x$ atomic orbital of one atom approaches the $2p_x$ atomic orbital of another atom, the overlapping occurs sidewise and not end-to-end. *The molecular orbital formed by sidewise or lateral overlap is known as pi (π) molecular orbital.* The molecular orbital formed is not symmetrical about the internuclear axis. The molecular orbital formed by overlapping of two $2p_x$ atomic orbitals by the addition of electron waves is called *bonding pi molecular orbital* designated as $\pi 2p_x$ while the molecular orbital formed by the overlapping of two $2p_x$ atomic orbitals by the subtraction of electron waves is called *antibonding molecular orbital* labelled as $\pi^* 2p_x$. These are shown in Fig. 53.

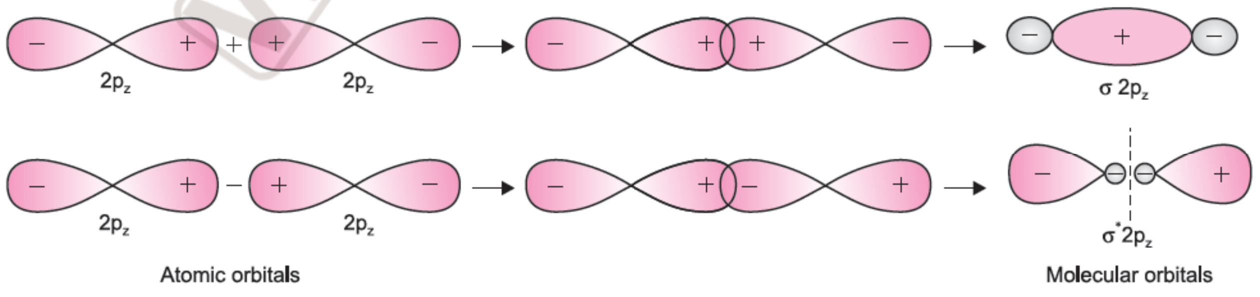


Fig. 52. Bonding ($\sigma 2p_z$) and antibonding ($\sigma^* 2p_z$) molecular orbitals from $2p_z$ atomic orbitals.

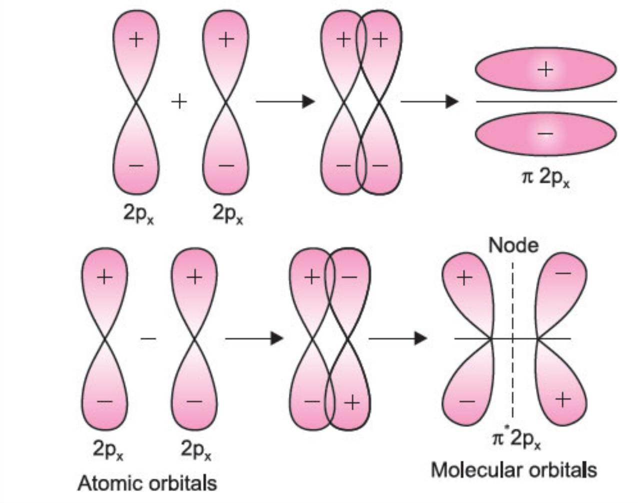


Fig. 53. Bonding ($\pi 2p_x$) and antibonding ($\pi^* 2p_x$) molecular orbitals from $2p_x$ atomic orbitals.

Similarly, when a $2p_y$ orbital of one atom overlaps with a $2p_y$ orbital of another atom, they also overlap sidewise forming two molecular orbitals $\pi 2p_y$ and $\pi^* 2p_y$. These are exactly similar to $\pi 2p_x$ and $\pi^* 2p_x$ MOs.

Differences between σ and π Molecular Orbitals

σ MO	π MO
1. It is formed by the head-to-head overlap of AOs *i.e,* along internuclear axis.	It is formed by sidewise overlap of AOs perpendicular to internuclear axis.
2. The overlap region is maximum.	The overlap region is minimum.
3. The orbital is symmetrical to rotation about internuclear axis.	The orbital is not symmetrical to rotation about internuclear axis.
4. It leads to the formation of a strong bond.	It leads to the formation of a weak bond.

CONDITIONS FOR THE COMBINATION OF ATOMIC ORBITALS

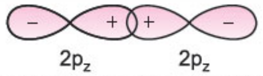
Molecular orbitals are formed by the combination of atomic orbitals. But all types of orbitals cannot combine with each other. The following are the **main conditions for effective combination of atomic orbitals :**

1. ***The combining atomic orbitals must have same or nearly the same energies.*** For example, in case of homonuclear diatomic molecules of the type A_2, 2*s*-orbital of one atom can combine with 2*s*-orbital of another atom but 1*s*-orbital of one atom cannot combine with 2*s*-orbital of another atom.

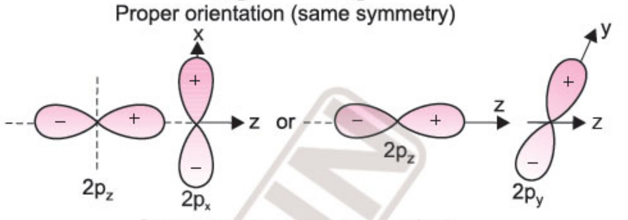
2. ***The extent of overlapping between the atomic orbitals of two atoms should be large.*** Greater the extent of overlap, the greater will be the electron density between the nuclei of a molecular orbital.

3. ***The combining atomic orbitals must have the same symmetry (or proper orientation) about the moecular axis.***

For example, if we take *z*-axis as the internuclear axis, $2p_z$ orbital of one atom can combine with $2p_z$ orbital of other atom but $2p_z$ orbital of one atom cannot combine with $2p_x$ or $2p_y$ orbitals of other atom because of their different orientations or symmetries.



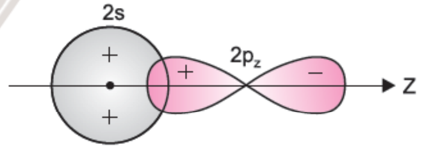
Proper orientation (same symmetry)



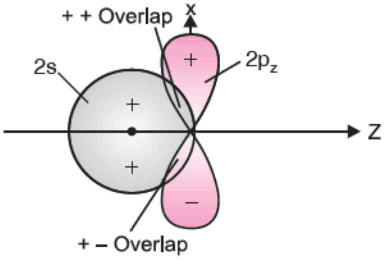
Improper orientation (no overlap)

Fig. 54. Possibility of combination of $2p_z$ and $2p_z$ and impossibility of combination of $2p_z$ and $2p_x$ or $2p_z$ and $2p_y$.

Similarly a 2*s*-orbital of one atom can combine with $2p_z$ orbital of another atom [Fig. 55(a)] but it cannot overlap with $2p_x$ or $2p_y$ orbital of another atom. When 2*s*-orbital of one atom A overlaps with $2p_x$ orbital of another atom B [Fig. 55(b)], ++ overlap is cancelled by the + – overlap. As a result, no molecular orbital is formed. In other words, such a combination (2*s* with $2p_x$ or 2*s* with $2p_y$) is not possible.



(a) Same symmetry (++ overlap possible)



(b) Improper overlap (no net overlap)

Fig. 55. Possibility of combination of 2*s* and $2p_z$ atomic orbitals and absence of combination of 2*s* and $2p_x$ atomic orbitals.

SOLVED EXAMPLES

❑ **Example 15.**

Label the molecular orbitals formed by the following combinations of atomic orbitals (Assume z-axis as internuclear axis) :

(*i*) $2s + 2s$ (*ii*) $2p_x - 2p_x$ (*iii*) $2p_z + 2p_z$

(*iv*) $1s - 1s$ (*v*) $2p_y + 2p_y$.

Solution : The MOs formed are :

(*i*) $2s + 2s = \sigma 2s$ (*ii*) $2p_x - 2p_x = \pi^* 2p_x$

(*iii*) $2p_z + 2p_z = \sigma 2p_z$ (*iv*) $1s - 1s = \sigma^* 1s$

(*v*) $2p_y + 2p_y = \pi 2p_y$

Practice Problems

18. If z-axis is the internuclear axis, which of the following combinations are not allowed ?

(*i*) $2s$ and $2s$ (*ii*) $1s$ and $2p_x$ (*iii*) $2p_y$ and $2p_y$
(*iv*) $2p_x$ and $2p_z$ (*v*) $2p_z$ and $2p_z$ (*vi*) $2s$ and $2p_z$
(*vii*) $2p_x$ and $2p_y$.

19. Which of the following combinations of atomic orbitals will give antibonding π-molecular orbital (assume z-axis as internuclear axis):

(*i*) $2s + 2p_z$ (*ii*) $2p_y + 2p_y$ (*iii*) $2p_x - 2p_x$ (*iv*) $2p_z - 2p_z$.

Answers to Practice Problems

18. (*ii*), (*iv*), (*vii*) **19.** (*iii*)

ENERGY LEVEL DIAGRAM FOR MOLECULAR ORBITALS

The relative energies of molecular orbitals depend upon the following two factors :

(*i*) the energies of the AOs combining to form MOs.

(ii) the extent of overlapping between the atomic orbitals. The greater the overlap, the more the bonding orbital is lowered and the anti-bonding orbital is raised in energy relative to AOs. For example, the extent of overlapping in case of σ-orbital is more than that in π-orbital. Consequently, the energy of $\sigma\ 2p_z$ is lower than the energy of bonding $\pi\ 2p_x$ or $\pi\ 2p_y$ MOs.

Now, $1s$ AOs of two atoms form two MOs designated as $\sigma 1s$ and σ^*1s. The $2s$ and $2p$ orbitals (eight AOs on two atoms) form four bonding MOs and four anti-bonding MOs as :

Bonding MOs : $\sigma 2s, \sigma 2p_z, \pi 2p_x, \pi 2p_y$

Anti-bonding MOs : $\sigma^*2s, \sigma^*2p_z, \pi^*2p_x, \pi^*2p_y$

The energy levels of these molecular orbitals have been determined experimentally by spectroscopic methods. The order of increasing energy of molecular orbitals obtained by the combination of $1s$, $2s$ and $2p$ orbitals of two atoms is :

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

Energy increases

However, experimental evidence for some diatomic molecules have shown that above sequence of energy levels of MOs is not correct for all molecules. For example, for homonuclear diatomic molecules of second row elements such as Li_2, Be_2, B_2, C_2, N_2, **the $\sigma 2p_z$ MO is higher in energy than $\pi 2p_x$ and $\pi 2p_y$ MOs.** The order of MOs for these molecules is

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

Energy increases

But for molecules O_2 onwards (O_2, F_2), the first order of energies of MOs is correct.

Thus, for diatomic molecules of second period (Li_2 to Ne_2), there are two types of energy levels of MOs as shown in Fig. 56. For molecules Li_2, Be_2, B_2, C_2 and N_2 the molecular orbital energy level diagram is shown in Fig. 56 (*a*). On the other hand, for the molecules O_2, F_2 and Ne_2 the molecular orbital energy level diagram is shown in Fig. 56 (*b*).

The main difference between the two types of sequences is that for molecules O_2, F_2 and Ne_2, the $\sigma 2p_z$ MO is lower in energy than $\pi 2p_x$ and $\pi 2p_y$ MOs while in the case of molecules Li_2, Be_2, B_2, C_2 and N_2, $\sigma 2p_z$ MO has higher energy than $\pi 2p_x$ and $\pi 2p_y$ MOs.

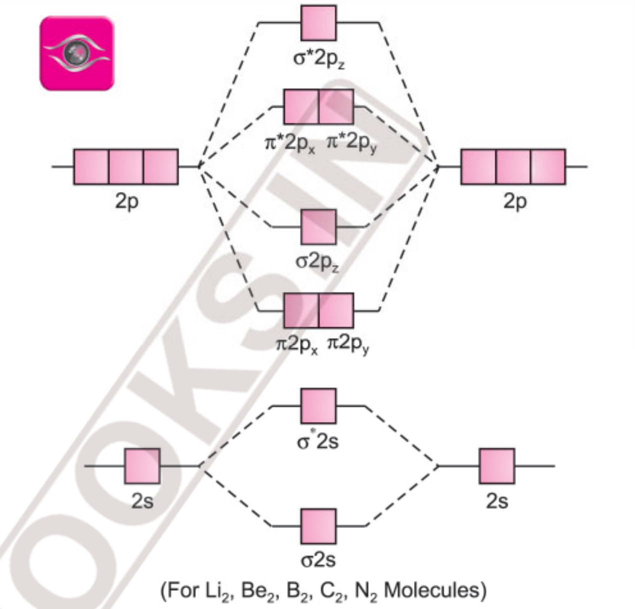


Fig. 56. (*a*) Molecular orbital energy level diagram for Li_2, Be_2, B_2, C_2 and N_2 molecules.

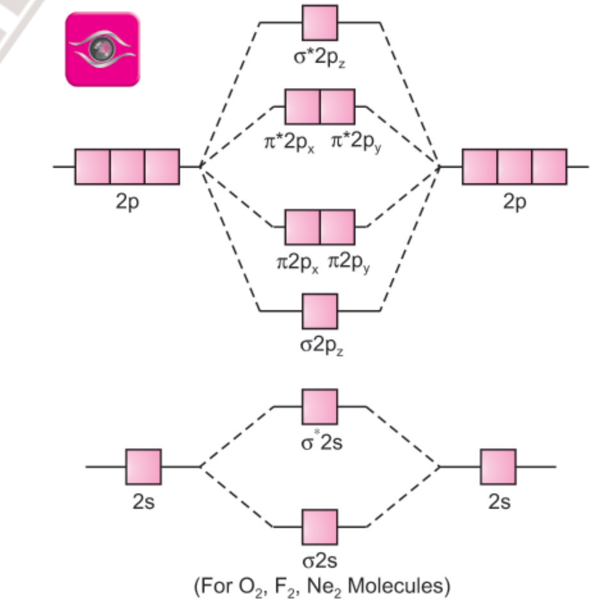


Fig. 56. (*b*) Molecular orbital energy level diagram for O_2, F_2 and Ne_2 molecules.

The main reason for the difference in sequences is the interaction of $2s$ and $2p_z$ AOs. For the molecules Li_2, Be_2, B_2, C_2 and N_2, the differences in energies of $2s$ and $2p_z$ orbitals is small and, therefore, they can interact. While the energies of $2s$ and $2p_z$ AOs for O_2, F_2 and Ne_2 is large and therefore, they cannot interact. The discussion is beyond the scope of the present book.

RULES FOR FILLING MOLECULAR ORBITALS

The following rules are followed for filling up molecular orbitals with electrons in order to write molecular configurations :

1. The molecular orbital having the lowest energy is filled first. This is in accordance with ***Aufbau principle*** as already discussed for atoms.
2. Each molecular orbital can accommodate maximum of two electrons having opposite spins. This is in accordance with ***Pauli's exclusion principle.***
3. If there are two molecular orbitals of the same energy, the pairing of electrons will occur only after each orbital of same energy has one electron. This is in accordance with ***Hund's rule.***

ELECTRONIC CONFIGURATIONS AND MOLECULAR BEHAVIOUR

The distribution of electrons among various molecular orbitals is called the **electronic configuration of the molecule.** The electronic configuration of the molecule or the molecular orbital energy level diagram gives the following information, regarding the behaviour of molecules.

(*a*) Stability of a molecule. The electrons in bonding molecular orbitals will give stability to the molecule whereas those in antibonding molecular orbitals will decrease the stability. Thus, if N_b represents the number of electrons in bonding molecular orbitals and N_a represents the number of electrons in anti-bonding molecular orbitals, then the following generalization can be made :

(*i*) The molecule is stable if $N_b > N_a$.

(*ii*) The molecule is unstable if $N_b < N_a$.

(*iii*) The molecule is unstable if $N_b = N_a$.

- According to (*i*), more bonding molecular orbitals are occupied and therefore, the bonding influence is stronger and therefore, a stable molecule is formed.
- In (*ii*), the anti-bonding influence is stronger and hence the molecule is unstable.
- According to (*iii*), even if the number of electrons in bonding MOs and the number of electrons in anti-bonding MOs are same, the atoms do not combine to form molecules. *This is because of the fact that the effect of anti-bonding electrons is slightly more than that of bonding electrons.*

(b) Bond order. It is defined *as the number of covalent bonds in a molecule.* It is equal to **one half of the difference between the number of electrons in the bonding and antibonding molecular orbitals.**

Bond order

$$= \frac{\begin{bmatrix}\text{No. of electrons}\\ \text{in bonding MOs}\end{bmatrix} - \begin{bmatrix}\text{No. of electrons}\\ \text{in anti-bonding MOs}\end{bmatrix}}{2}$$

or $$= \frac{N_b - N_a}{2}$$

The bond orders of 1, 2 or 3 correspond to single, double or triple bond. But bond order may be fractional also in some cases.

Information Conveyed by Bond Order

The bond order conveys the following important informations :

(*i*) If the value of bond order is positive, it indicates a stable molecule and if the value of bond order is negative or zero, it means that the molecule is unstable.

(*ii*) The stability of a molecule is measured by its bond dissociation energy. But *the bond dissociation energy is directly proportional to the bond order.* **Greater the bond order, greater is the bond dissociation energy.** For example, nitrogen molecule with bond order equal to 3 has larger bond dissociation energy (945 kJ mol^{-1}) than oxygen molecule (bond dissociation energy 495 kJ mol^{-1}) with a bond order equal to 2.

(*iii*) Bond order is inversely proportional to the bond length. The higher the bond order value, smaller is the bond length. For example, the bond length in nitrogen molecule is shorter than in oxygen molecule as shown below :

Molecule	Bond order	Bond Dissociation energy	Bond length
Oxygen	2	495 kJ mol^{-1}	121 pm
Nitrogen	3	945 kJ mol^{-1}	110 pm

(*c*) Magnetic character. If all the electrons in the molecule of a substance are paired, the substance is **diamagnetic** (repelled by the magnetic field)**.** On the other hand, if there are unpaired electrons in the molecule, the substance is **paramagnetic** (attracted by the magnetic field).

BONDING IN SOME DIATOMIC MOLECULES

Let us discuss bonding in some homonuclear diatomic molecules of the elements of first and second rows of the periodic table.

1. Hydrogen molecule (H_2). Each hydrogen atom has one electron in 1*s*-orbital and, therefore, there are two electrons in hydrogen molecule. Both these electrons are to be accommodated in the lowest energy molecular orbital. According to Pauli's exclusion principle, these two electrons should have opposite spins. The molecular orbital energy level diagram for H_2 molecule is shown in Fig. 57.

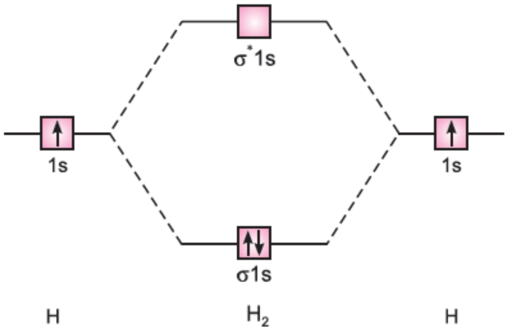


Fig. 57. Molecular orbital energy level diagram for H_2 molecule.

The molecular orbital electronic configuration of H_2 molecule is :

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

The bond order in H_2 is :

$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{2-0}{2} = 1$$

The bond dissociation energy of hydrogen molecule has been found to be 438 kJ mol^{-1} and bond length equal to 74 pm. Moreover, since no unpaired electron is present in hydrogen molecule, it is **diamagnetic.**

2. Hydrogen molecule ion (H_2^+). This is formed by the combination of hydrogen atom containing one electron and hydrogen ion having no electron. Therefore, this ion has only one electron. The molecular orbital diagram is given in Fig. 58.

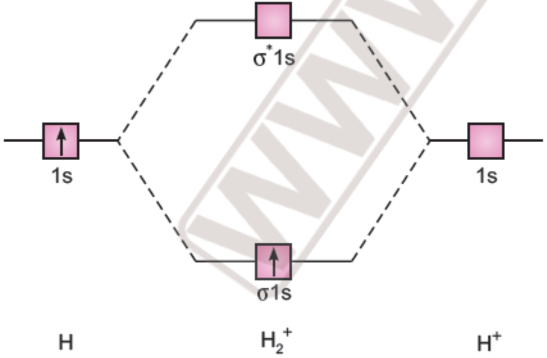


Fig. 58. Molecular orbital energy level diagram for H_2^+ ion.

The electronic configuration of the molecule ion is:

$$H_2^+ : (\sigma\ 1\ s)^1$$

$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{1-0}{2} = \frac{1}{2}$$

The positive value of bond order indicates that the molecule is stable. The presence of unpaired electron in the molecule indicates that it is **paramagnetic** molecule.

The bond length of H_2^+ ion is larger than that of H_2 molecule (bond length H_2^+ = 104 pm; H_2 = 74 pm) while its bond dissociation energy is less than that of H_2 molecule (bond dissociation energy H_2^+ = 269 kJ mol^{-1}, H_2 = 458 kJ mol^{-1}). *This clearly supports the fact that bond in H_2^+ ion is weaker than that in H_2 molecule.*

3. Hypothetical helium molecule (He_2). Each helium atom has two electrons in 1*s*-orbital, and therefore, there are four electrons in He_2 molecule. These electrons will be accommodated in σ1*s* and σ*1*s* MOs as shown in Fig. 59. The electronic configuration for helium molecule may be written as :

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

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

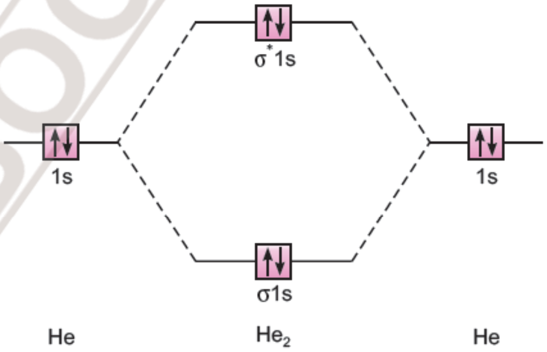


Fig. 59. Molecular orbital energy level diagram for He_2 molecule (hypothetical).

The **zero bond order value indicates that there is no net bonding and He_2 molecule should not be formed.** In fact, there is no experimental evidence for the existence of this molecule.

4. Helium molecule ion (He_2^+). This molecule contains three electrons, two from one helium atom and one from the other (He^+ ion). The molecular orbital electronic configuration of the molecule ion is

$$He_2^+ : (\sigma\ 1s)^2\ (\sigma^*\ 1s)^1$$

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

The value of bond order indicates that He_2^+ is stable. Its bond dissociation energy has been found to be 242 kJ mol^{-1}. The molecule is expected to be **paramagnetic** and the same has been experimentally observed also.

5. Lithium molecule (Li_2). The electronic configuration of lithium is $1s^2 2s^1$. There are six electrons in lithium molecule. The electronic configuration of Li_2 molecule may be written as :

$$Li_2 : (\sigma 1s)^2\, (\sigma 1s^*)^2\, (\sigma 2s)^2$$

The above configuration may also be written as :

$$\text{KK}\ (\sigma 2s)^2$$

where KK represents fully filled inner K shells in two atoms i.e. $(\sigma 1s)^2\,(\sigma 1^*s)^2$

From the electronic configuration of Li_2 molecule, it is clear that there are 4 electrons in bonding MOs and 2 electrons in antibonding MOs.

Therefore, its bond order is :

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

Thus, there is one Li—Li sigma bond. The bond energy of the molecule is quite low, being about 110 kJ mol^{-1}. The bond length of the molecule is 265 pm. Since it has no unpaired electrons, it should be diamagnetic. Indeed diamagnetic Li_2 molecules are known to exist in the vapour phase.

Comparison of Li—Li and H—H bonds. The comparison of Li—Li and H—H bonds reveals that the sigma bond in Li_2 molecule is weaker and much longer than σ-bond in H_2 molecule. This may be attributed to the following reasons :

(*i*) The 2*s* orbital of lithium is bigger in size than the 1*s* orbital. Therefore, the overlapping of 2*s*—2*s* atomic orbitals is less effective than the overlapping of 1*s*—1*s* orbitals.

(*ii*) In lithium molecule, the outer electrons in (σ2*s*) molecular orbital are shielded by the inner 1*s* electrons. Therefore, the attraction between the nuclei and the electrons in (σ2*s*) molecular orbital is less.

Moreover, the inner $1s^2$ electrons of two lithium atoms cause repulsion between the atoms. Therefore, they do not allow them to come closer.

6. Beryllium molecule, (Be_2). Beryllium (Z = 4) has electronic configuration $1s^2 2s^2$. In the formation of a diatomic molecule, evidently, two outer electrons of each atom, *i.e.*, four in all, have to be accommodated in molecular orbitals. Two of these go into the bonding (σ2*s*) orbital while the other two have to go into the anti-bonding (σ*2*s*) orbital.

The molecular orbital electronic configuration is :

$$Be_2 : \text{KK}(\sigma 2s)^2\,(\sigma^* 2s)^2$$

$$\text{bond order} = \frac{1}{2}(2-2) = 0$$

The **zero bond order** suggests that Be_2 molecule does not exist.

7. Boron molecule, (B_2). The electronic configuration of boron is $1s^2\ 2s^2\ 2p^1$. The outermost shell of each atom contains 3 electrons. When two B atoms combine to form molecule B_2, there are 6 electrons which need to be accommodated in the molecular orbitals of B_2. The molecular orbital electronic configuration is :

$$B_2 : \text{KK}(\sigma 2s)^2\,(\sigma^* 2s)^2\,(\pi 2p_x)^1\,(\pi 2p_y)^1$$

$$\text{bond order} = \frac{1}{2}(4-2) = 1$$

The molecule has only one bond. The electrons which contribute towards bonding are the $\pi 2p_x$ and $\pi 2p_y$ MOs. This indicates that the molecule is formed by a weak π-bond. The bond dissociation energy of B_2 molecule has been found to be 290 kJ mol^{-1} and bond length equal to 159 pm.

Since each $\pi 2p_x$ and $\pi 2p_y$ MO contains single electron, the molecule B_2 is **paramagnetic.**

8. Carbon molecule, (C_2). The electronic configuration of carbon is $1s^2\ 2s^2\ 2p^2$. The outer shell of each atom contains 4 electrons. In the formation of C_2 molecule, there will be evidently 8 electrons to be accommodated in the outer molecular orbitals of C_2. The molecular orbital electronic configuration is :

$$C_2 : \text{KK}\,(\sigma 2s)^2\ \ (\sigma^* 2s)^2\,(\pi 2p_x)^2\,(\pi 2p_y)^2$$

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

Thus, the C_2 molecule has two bonds. The bond dissociation energy of C_2 molecule has been found to be 620 kJ mol^{-1} and bond length equal to 131 pm.

Further, since C_2 molecule does not have any unpaired electron, it is ***diamagnetic.*** The diamagnetic C_2 molecule has been detected in vapour phase.

It may be noted that double bond in C_2 molecule consists of both the *pi* bonds because of the presence of 4 electrons in two *pi* MOs. In most of the other molecules, a double is made up of a sigma bond and a *pi* bond.

9. Nitrogen molecule (N_2). The electronic configuration of nitrogen atom is $1s^2\ 2s^2\ 2p_x^{\ 1}\ 2p_y^{\ 1}\ 2p_z^{\ 1}$ and N_2 molecule has 14 electrons. The M.O. diagram is shown in Fig. 60.

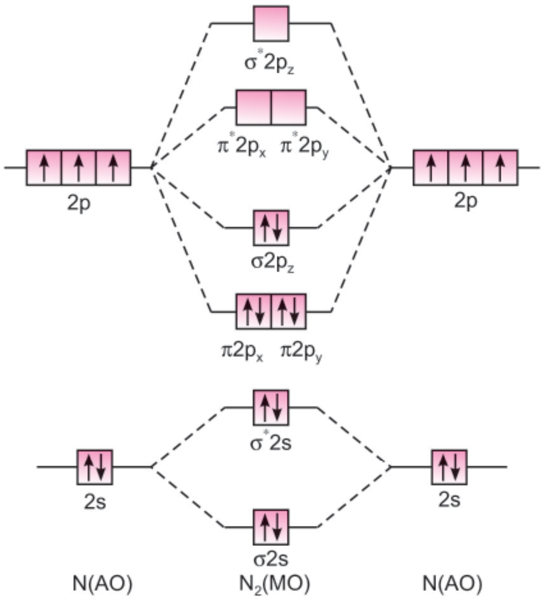


Fig. 60. Molecular orbital energy level diagram for N_2 molecule.

The molecular orbital electronic configuration of the molecule is :

$$N_2 : KK\,(\sigma 2s)^2\,(\sigma^* 2s)^2\,(\pi 2p_x)^2\,(\pi 2p_y)^2\,(\sigma 2p_z)^2$$

$$\text{Bond order} = \frac{8-2}{2} = 3.$$

Thus, nitrogen molecule has **three bonds,** one σ and two π-bonds. This is in accordance with very high bond dissociation energy (945 kJ mol^{-1}) and small bond length (110 pm) of the molecule. The molecule is **diamagnetic** because there are no unpaired electrons.

Comparison of N_2 and N_2^+ ion

N_2^+ ion is formed by the removal of one electron from N_2 molecule. This electron will be lost from $2p_z$ M.O. Hence the electronic configuration of N_2^+ ion will be

$$N_2^+ : KK\,(\sigma 2s)^2\,(\sigma^* 2s)^2\,(\pi 2p_x)^2\,(\pi 2p_y)^2\,(\sigma 2p_z)^1$$

$$\text{Bond order} = \frac{7-2}{2} = 2\frac{1}{2}$$

Since bond order of N_2^+ ion (2.5) is less than the bond order of N_2 (3) molecule, therefore, the bond strength of N_2^+ will be less than that of N_2 molecule and bond length of N_2^+ will be more than that of N_2 molecule.

10. Oxygen molecule (O_2). The electronic configuration of oxygen atom is $1s^2\,2s^2\,2p_x^2\,2p_y^1\,2p_z^1$. Therefore, oxygen molecule has 16 electrons. In the formation of molecular orbitals, the electrons in the inner shells are expressed as KK denoting $(\sigma 1s)^2\,(\sigma^* 1s)^2$. The remaining 12 electrons are filled in molecular orbitals as shown in Fig. 61.

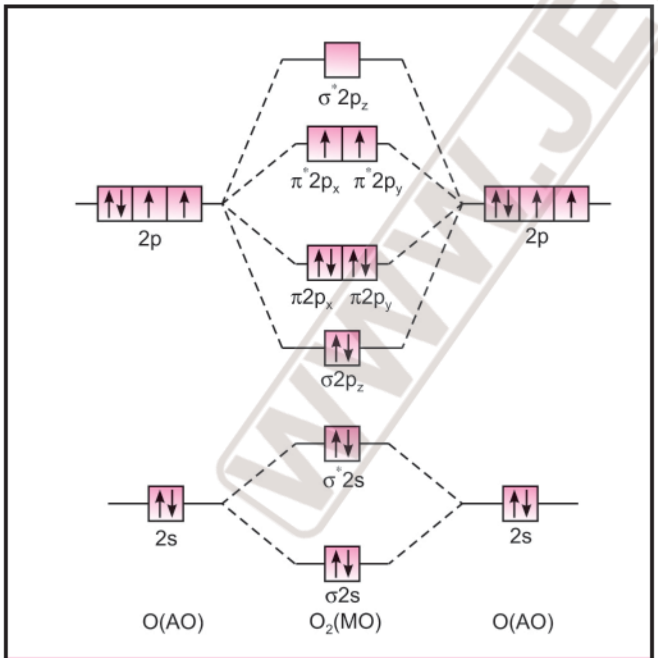


Fig. 61. Molecular orbital energy level diagram for O_2 molecule.

The electronic configuration of the molecule is :

$$O_2 : KK\,(\sigma 2s)^2\,(\sigma^* 2s)^2\,(\sigma 2p_z)^2\,(\pi 2p_x)^2\,(\pi 2p_y)^2\,(\pi^* 2p_x)^1\,(\pi^* 2p_y)^1$$

$$\text{Bond order} = \frac{8-4}{2} = 2$$

Thus, oxygen molecule has **two bonds** (one σ and one π). Further, in accordance with Hund's rule, the last two electrons in $\pi^* 2p_x$ and $\pi^* 2p_y$ orbitals will remain unpaired. Therefore, the molecule has **paramagnetic character** due to the presence of two unpaired electrons. These facts are in accordance with experimental observations. The bond dissociation energy in O_2 molecule has been found to be 498 kJ mol^{-1} and bond length 121 pm.

Comparison of O_2, O_2^+, O_2^- and O_2^{2-} species

Oxygen molecule ion (O_2^+). This ion is formed by the removal of one electron from O_2 molecule as :

$$O_2 \longrightarrow O_2^+ + e^-$$

It is clear from Fig. 61, that the electron will be lost from anti-bonding MO *i.e.* $\pi^* 2p_y$ and electronic configuration of O_2^+ is :

$$O_2^+ : KK\,(\sigma 2s)^2\,(\sigma^* 2s)^2\,(\sigma 2p_z)^2\,(\pi 2p_x)^2\,(\pi 2p_y)^2\,(\pi^* 2p_x)^1$$

$$\text{Bond order} = \frac{8-3}{2} = \frac{5}{2} = 2\frac{1}{2}$$

Since the bond order of O_2^+ ion is greater than the bond order of O_2 molecule, therefore, the ***bond strength of O_2^+ will be more than that of O_2 molecule and bond length of O_2^+ will be less than that of O_2 molecule.***

Superoxide ion (O_2^-). This ion is formed by the addition of one electron as :

$$O_2 + e^- \longrightarrow O_2^-$$

According to Fig. 61, the electron will be added to either of the antibonding MO (*s*) ($\pi^* 2p_x$ or $\pi^* 2p_y$). The electronic configuration of O_2^- is

$$O_2^- : KK\,(\sigma 2s)^2\,(\sigma^* 2s)^2\,(\sigma 2p_z)^2\,(\pi 2p_x)^2\,(\pi 2p_y)^2\,(\pi^* 2p_x)^2\,(\pi^* 2p_y)^1$$

$$\text{Bond order} = \frac{8-5}{2} = \frac{3}{2} = 1\frac{1}{2}$$

Since the bond order of O_2^- ion is less than that of O_2 molecule, therefore, **the bond in O_2^- will be weaker than in O_2 and bond length of O_2^- will be larger than that of O_2 molecule.**

Peroxide ion (O_2^{2-}). This ion is formed by the addition of two electrons to O_2 molecule.

$$O_2 + 2e^- \longrightarrow O_2^{2-}$$

The additional electrons enter the two half-filled π-anti-bonding MOs. The electronic configuration of O_2^{2-} ion is :

$$O_2^{2-} : KK\,(\sigma 2s)^2\,(\sigma^* 2s)^2\,(\sigma 2p_z)^2\,(\pi 2p_x)^2\,(\pi 2p_y)^2\,(\pi^* 2p_x)^2\,(\pi^* 2p_y)^2$$

$$\text{Bond order} = \frac{8-6}{2} = 1$$

Since bond order of O_2^{2-} ion is less than that of O_2 molecule, therefore, ***the bond O_2^{2-} will be weaker than in O_2 and bond length of O_2^{2-} will be larger than that of O_2 molecule.***

The experimental bond dissociation energies and bond lengths for O_2, O_2^+ and O_2^- are given below :

Species	**Bond order**	**Bond dissociation energy (kJ mol⁻¹)**	**Bond length**
O_2^+	$2\frac{1}{2}$	625	112 pm
O_2	2	495	121 pm
O_2^-	$1\frac{1}{2}$	395	130 pm

The species O_2, O_2^+, O_2^- and O_2^{2-} can be arranged as:
Bond dissociation energy : $O_2^+ > O_2 > O_2^- > O_2^{2-}$
Bond length : $O_2^{2-} > O_2^- > O_2 > O_2^+$

11. Fluorine molecule (F_2). The electronic configuration of fluorine atom is $1s^2\ 2s^2\ 2p^5$ and therefore, there are 14 electrons in the valence shell of F_2 molecule. The molecular orbital electronic configuration of the molecule is :

F_2 : KK $(\sigma 2s)^2\ (\sigma^* 2s)^2\ (\sigma 2p_z)^2\ (\pi 2p_x)^2\ (\pi 2p_y)^2\ (\pi^* 2p_x)^2\ (\pi^* 2p_y)^2$

$$\text{Bond order} = \frac{8-6}{2} = 1.$$

Thus, there is one σ-**bond** in the molecule. Since all the electrons in the molecular orbitals are paired, it is **diamagnetic.** The single bond in the molecule is also in agreement with bond dissociation energy of 159 kJ mol⁻¹ and bond length equal to 143 pm.

12. Hypothetical neon molecule. The electronic configuration of neon atom is $1s^2\ 2s^2\ 2p^6$ and the molecular orbital electronic configuration of neon molecule is

F_2 : KK $(\sigma 2s)^2\ (\sigma^* 2s)^2\ (\sigma 2p_z)^2\ (\pi 2p_x)^2\ (\pi 2p_y)^2\ (\pi^* 2p_x)^2\ (\pi^* 2p_y)^2\ (\sigma^* 2p_z)^2$

$$\text{Bond order} = \frac{8-8}{2} = 0.$$

Thus, Ne_2 molecule **does not exist.**

SOLVED EXAMPLES

☐ Example 16.

Arrange the following species in the decreasing order of their bond dissociation enthalpies :

O_2, O_2^+ and O_2^-.

Solution : The bond dissociation enthalpy of a molecule is related to its bond order. The larger the bond order, the greater will be the bond dissociation enthalpy. We shall first calculate the bond orders for the various species from their electronic configurations.

O_2 : KK $(\sigma 2s)^2\ (\sigma^* 2s)^2\ (\sigma 2p_z)^2\ (\pi 2p_x)^2\ (\pi 2p_y)^2\ (\pi^* 2p_x)^1\ (\pi^* 2p_y)^1$

$$\therefore \quad \text{Bond order} = \frac{8-4}{2} = 2.$$

O_2^+ : KK $(\sigma 2s)^2\ (\sigma^* 2s)^2\ (\sigma 2p_z)^2\ (\pi 2p_x)^2\ (\pi 2p_y)^2\ (\pi^* 2p_x)^1$

$$\therefore \quad \text{Bond order} = \frac{8-3}{2} = 2\frac{1}{2}$$

O_2^- : KK $(\sigma 2s)^2\ (\sigma^* 2s)^2\ (\sigma 2p_z)^2\ (\pi 2p_x)^2\ (\pi 2p_y)^2\ (\pi^* 2p_x)^2\ (\pi^* 2p_y)^1$

$$\therefore \quad \text{Bond order} = \frac{8-5}{2} = 1\frac{1}{2}$$

Now, O_2^+ has the highest bond order, it will have largest bond dissociation enthalpy. The bond dissociation enthalpies will decrease in the order $O_2^+ > O_2 > O_2^-$.

☐ Example 17.

With the help of M.O. theory, predict which of the following species is diamagnetic : H_2^+, O_2, O_2^{2+}

Solution : The diamagnetic species are those which contain only paired electrons. This can be predicted from the molecular orbital electronic configurations as given below :

H_2^+ : $(\sigma 1s)^1$

O_2 : KK $(\sigma 2s)^2\ (\sigma^* 2s)^2\ (\sigma 2p_z)^2\ (\pi 2p_x)^2\ (\pi 2p_y)^2\ (\pi^* 2p_x)^1\ (\pi^* 2p_y)^1$

O_2^{2+} : KK $(\sigma 2s)^2\ (\sigma^* 2s)^2\ (\sigma 2p_z)^2\ (\pi 2p_x)^2\ (\pi 2p_y)^2$

Since O_2^{2+} contain all paired electrons, it will be diamagnetic.

☐ Example 18.

Explain why N_2 has greater bond dissociation energy than N_2^+ whereas O_2 has lesser bond dissociation energy than O_2^+.

Solution: The M.O. electronic configurations are :

N_2 : KK$(\sigma 2s)^2\ (\sigma^* 2s)^2\ (\pi 2p_x)^2\ (\pi 2p_y)^2\ (\sigma 2p_z)^2$

$$\text{Bond order} = \frac{8-2}{2} = 3$$

N_2^+ : KK $(\sigma 2s)^2\ (\sigma^* 2s)^2\ (\pi 2p_x)^2\ (\pi 2p_y)^2\ (\sigma 2p_z)^1$

$$\text{Bond order} = \frac{7-2}{2} = 2\frac{1}{2}$$

Since bond order of N_2 is larger than that of N_2^+, N_2 has greater bond dissociation energy than N_2^+.

O_2 : KK$(\sigma 2s)^2\ (\sigma^* 2s)^2\ (\sigma 2p_z)^2\ (\pi 2p_x)^2\ (\pi 2p_y)^2\ (\pi^* 2p_x)^1\ (\pi^* 2p_y)^1$

$$\text{Bond order} : \frac{8-4}{2} = 2$$

O_2^+ : KK $(\sigma 2s)^2\ (\sigma^* 2s)^2\ (\sigma 2p_z)^2\ (\pi 2p_x)^2\ (\pi 2p_y)^2\ (\pi^* 2p_x)^1$

$$\text{Bond order} = \frac{8-3}{2} = 2\frac{1}{2}$$

Since bond order of O_2 is less than that of O_2^+, O_2 has lower bond dissociation energy than O_2^+.

☐ Example 19.

Which of the two : peroxide ion or superoxide ion has larger bond length ?

Solution: The bond length of a molecule is related to its bond order. The larger the bond order, the smaller will be the bond length.

Superoxide ion, O_2^- :

O_2^- : KK $(\sigma 2s)^2\ (\sigma^* 2s)^2\ (\sigma 2p_z)^2\ (\pi 2p_x)^2\ (\pi 2p_y)^2\ (\pi^* 2p_x)^2\ (\pi^* 2p_y)^1$

$$\text{Bond order} = \frac{8-5}{2} = 1\frac{1}{2}$$

Peroxide ion, O_2^{2-} :

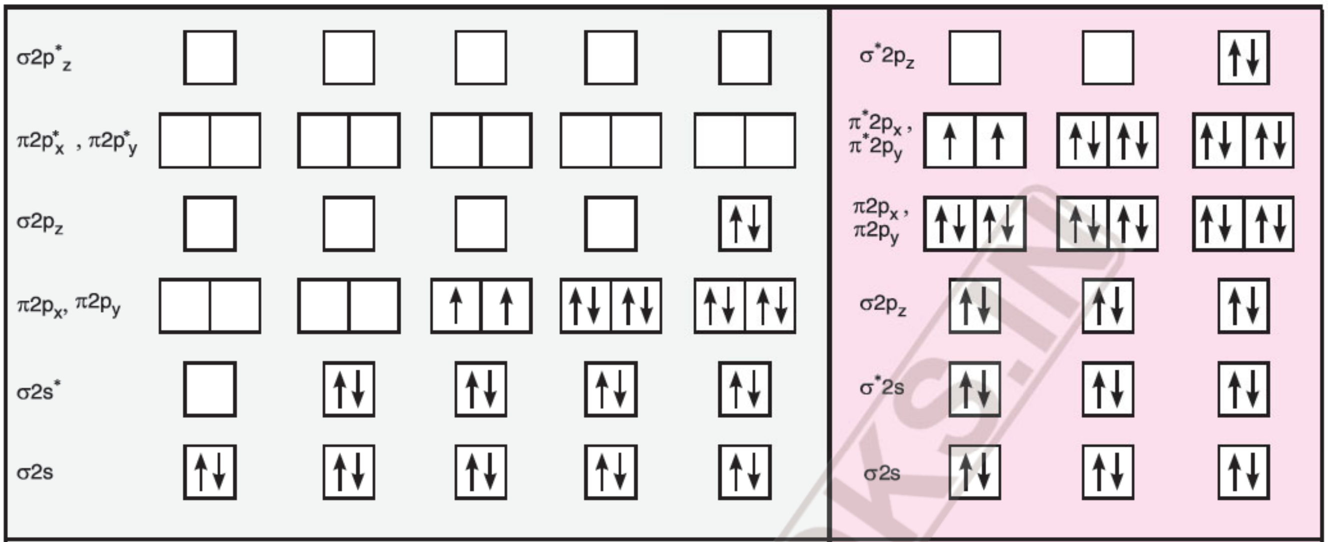
O_2^{2-} : KK $(\sigma 2s)^2\ (\sigma^* 2s)^2\ (\sigma 2p_z)^2\ (\pi 2p_x)^2\ (\pi 2p_y)^2\ (\pi^* 2p_x)^2\ (\pi^* 2p_y)^2$

$$\text{Bond order} = \frac{8-6}{2} = 1$$

Now, superoxide ion (O_2^-) has larger bond order than peroxide ion (O_2^{2-}), therefore, bond length of peroxide ion will be larger.

SUM UP

M.O. occupancy and molecular properties of homonuclear diatomic molecules of second period.



Molecule	Li_2	Be_2	B_2	C_2	N_2	O_2	F_2	Ne_2
Bond order	1	0	1	2	3	2	1	0
Bond energy (kJ mol^{-1})	110	–	290	620	945	498	159	–
Bond length (pm)	265	–	159	131	110	121	143	–
Paramagnetic (P) Diamagnetic (D)	D	–	P	D	D	P	D	–

MOLECULAR ORBITAL ELECTRONIC CONFIGURATIONS OF SOME COMMON HETERONUCLEAR MOLECULES

The configurations of heteronuclear molecules (containing different atoms) can be written in a similar manner as in case of homonuclear molecules.

(*i*) NO : Total number of electrons = 7 + 8 = 15

NO : KK$(\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p_x)^2(\pi 2p_y)^2(\sigma 2p_z)^2(\pi^* 2p_x)^1$

Bond order $= \frac{8-3}{2} = \mathbf{2\frac{1}{2}}$

(*ii*) NO^+ : KK $(\sigma 2s)^2\ (\sigma^* 2s)^2\ (\pi 2p_x)^2\ (\pi 2p_y)^2\ (\sigma 2p_z)^2$

Bond order $= \frac{8-2}{2} = \mathbf{3}$

(*iii*) **CN :** Total number of electrons = 6 + 7 = 13

CN : KK $(\sigma 2s)^2\ (\sigma^* 2s)^2\ (\pi 2p_x)^2\ (\pi 2p_y)^2\ (\sigma 2p_z)^1$

Bond order $= \frac{7-2}{2} = \mathbf{2\frac{1}{2}}$

(*iv*) CN^- : KK $(\sigma 2s)^2\ (\sigma^* 2s)^2\ (\pi 2p_x)^2\ (\pi 2p_y)^2\ (\sigma 2p_z)^2$

Bond order $= \frac{8-2}{2} = \mathbf{3}$

(*v*) **CO** : Total number of electrons = 6 + 8 = 14

CO : KK $(\sigma 2s)^2\ (\pi 2p_x)^2\ (\pi 2p_y)^2\ (\sigma 2p_z)^2\ (\sigma^* 2s)^2$

Bond order $= \frac{8-2}{2} = \mathbf{3}$

Summary of MO electronic configurations for some heteronuclear diatomic molecules.

Valence electrons	Species	MO electronic configuration	Bond order	Bond dissociation energy (kJ mol^{-1})	Bond length (Å)
8	BN	KK$(\sigma 2s)^2\ (\sigma^* 2s)^2\ (\pi 2p_x)^2\ (\pi 2p_y)^2$	2	385	128 pm
9	BO	KK$(\sigma 2s)^2\ (\sigma^* 2s)^2\ (\pi 2p_x)^2\ (\pi 2p_y)^2(\sigma 2p_z)^1$	$2\frac{1}{2}$	773	120 pm
	CN			786	117 pm
	*CO^+				111 pm
10	*CO NO^+	KK$(\sigma 2s)^2\ (\pi 2p_x)^2\ (\pi 2p_y)^2(\sigma 2p_z)^2\ (\sigma^* 2s)^2$	3	1067	113 pm 106 pm
11	NO	KK$(\sigma 2s)^2\ (\sigma^* 2s)^2\ (\pi 2p_x)^2\ (\pi 2p_y)^2\ (\sigma 2p_z)^2\ \ (\pi^* 2p_x)^1$	$2\frac{1}{2}$	667	115 pm

---

* It may be noted that in CO and CO^+, $\sigma^* 2s$ MO is higher in energy than $\pi 2p_x$, $\pi 2p_y$ and $\sigma 2p_z$ MOs and the configurations are, CO : KK$(\sigma\ 2s)^2\ (\pi 2p_x)^2(\pi 2p_y)^2(\sigma 2p_z)^2(\sigma^* 2s)^2$ and CO^+ : KK$(\sigma 2s)^2\ (\pi 2p_x)^2\ (\pi 2p_y)^2\ (\sigma 2p_z)^2(\sigma^* 2s)^1$

Practice Problems

- **20.** Which of the two : O_2^{2+} or O_2^{2-} is more stable ?
- **21.** Arrange the following in the increasing order of bond length : O_2, O_2^-, O_2^+
- **22.** Calculate the bond order in
  (*i*) H_2^+ (*ii*) H_2^- (*iii*) He_2^+ (*iv*) O_2^+
- **23.** Which two of H_2^+, H_2^- and H_2^{2-} have the same bond order ?
- **24.** Compare bond order in N_2 and N_2^+.
- **25.** Calculate the bond order of He_2^+ molecular ion.
- **26.** Write which out of O_2^+ and O_2^- is more stable.
- **27.** Indicate which one from O_2^- and O_2^{2-} may exhibit paramagnetism ?

Answers to Practice Problems

- **20.** O_2^{2+}
- **21.** $O_2^+ < O_2 < O_2^-$
- **22.** (*i*) $\frac{1}{2}$ (*ii*) $\frac{1}{2}$ (*iii*) $\frac{1}{2}$ (*iv*) $2\frac{1}{2}$
- **23.** H_2^+ and H_2^-
- **24.** Bond order in $N_2 = 3$, $N_2^+ = 2\frac{1}{2}$
- **25.** $\frac{1}{2}$
- **26.** O_2^+
- **27.** O_2^-

HYDROGEN BONDING

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

$$H — F \cdots\cdots H — F \cdots\cdots H — F \cdots$$

In other words, hydrogen atom acts as a bridge between two atoms, holding one atom by a covalent bond and the other atom by a hydrogen bond. The hydrogen bond is represented by dotted line (.....) while the covalent bond is represented by solid line (—). As a result of hydrogen bonding, HF exists as a cluster of hydrogen fluoride molecules and is represented as $(HF)_n$. Thus,

the attractive force which binds hydrogen atom of one molecule with electronegative atom (F, O or N) of another molecule is known as hydrogen bond or hydrogen bonding.

Strength of hydrogen bond. Hydrogen bond is much weaker than a covalent bond. The strength of hydrogen bond ranges from 10–40 kJ mol^{-1} while that of a normal covalent bond is of the order of 400 kJ mol^{-1}. Thus, a hydrogen bond is about one-tenth of the strength of a covalent bond. It may also be noted that the bond length of a hydrogen bond is larger than that of a covalent bond. For example, in case of HF molecule, the covalent bond between H and F is 109 pm while the bond length of hydrogen bond between F and H is 155 pm.

Cause of formation of hydrogen bond. When hydrogen is bonded to strongly electronegative element, A (such as F, O or N) the electron pair shared between the two atoms lies far away from the hydrogen atom. As a result, hydrogen atom becomes highly electropositive with respect to the other atom, A. Since the electrons are displaced towards A, it acquires partial negative charge (δ–) while hydrogen atom gets partial positive charge (δ+).

In other words, the bond H—A becomes polar and may be represented as $H^{\delta^+}—A^{\delta^-}$. The electrostatic force of attraction between positively charged hydrogen atom of one molecule and negatively charged atom of neighbouring molecule results in the formation of hydrogen bond. This may be represented as :

$$\cdots\overset{\delta^+}{H}—\overset{\delta^-}{A}\cdots\cdots\overset{\delta^+}{H}—\overset{\delta^-}{A}\cdots\cdots\overset{\delta^+}{H}—\overset{\delta^-}{A}\cdots$$

Conditions for Hydrogen Bonding

The following conditions are necessary for the formation of hydrogen bonding :

(*i*) **High electronegativity of atom bonded to hydrogen.** The molecule should contain an atom of high electronegativity such as F, O or N bonded to hydrogen atom. The common examples are HF, H_2O and NH_3.

(*ii*) **Small size of the electronegative atom.** The size of the electronegative atom should be quite small. This is due to the fact that the smaller the size of electronegative atom, the greater will be its attraction for the bonded electron pair. This will cause greater polarity in the bond between H and electronegative atom which results in stronger hydrogen bond. For example, NH_3 shows hydrogen bonding while HCl does not, although both N and Cl have the same electronegativity (3.0). Hydrogen bonds are not formed by Cl because of its bigger size than nitrogen.

Differences between hydrogen bond and covalent bond.

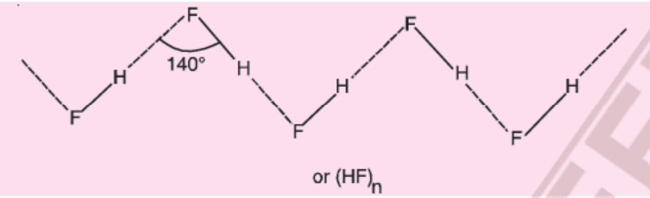
The main points of differences between hydrogen bond and covalent bond are :

Hydrogen bond	Covalent bond
1. Hydrogen bond involves dipole-dipole attractions.	1. Covalent bond involves sharing of electrons.
2. It is formed between hydrogen atom and a highly electronegative atom (F, O or N).	2. It is formed between any two electronegative atoms which may be of the same element or of different elements.
3. Strength of hydrogen bond is very small *e.g.* bond strength of H .... F bond is 41.83 kJ mol^{-1}.	3. Bond strength of covalent bond is sufficiently high. For example, bond strength of H–H bond is 433 kJ mol^{-1}.

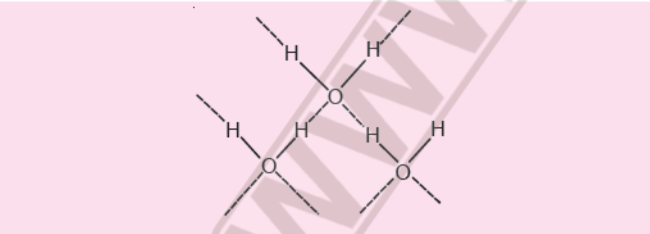
Examples of Hydrogen Bonded Compounds

A few examples of compounds which exhibit hydrogen bonding are discussed below :

1. Hydrogen fluoride. In the solid state, hydrogen fluoride consists of long zig-zag chains of molecules associated together through hydrogen bonds. Thus, hydrogen fluoride molecule is represented as $(HF)_n$. In the liquid or gaseous state, the chain however, becomes linear.

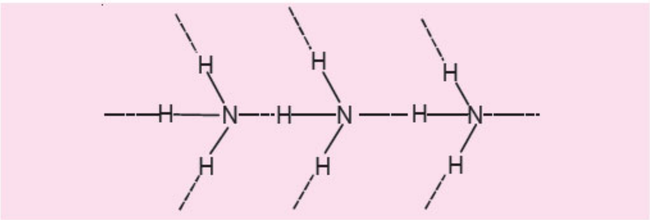


2. Water. Hydrogen bonding exists in water molecules also. In addition to two covalent (O—H) bonds in water, oxygen atom forms two hydrogen bonds. As a result of hydrogen bonds, each oxygen is tetrahedrally surrounded by four hydrogen atoms, two by covalent bonds and two by hydrogen bonds.



The associated water molecules may be expressed as $(H_2O)_n$.

3. Ammonia. Ammonia molecule has an electronegative nitrogen atom bonded to three hydrogen atoms. Due to difference in electronegativity between nitrogen and hydrogen, each hydrogen atom acquires positive charge. Thus, in the molecule, there is one negative site and three positive sites so that the molecules of ammonia associate through hydrogen bonding to form long chains.



Types of Hydrogen Bonds

Hydrogen bonds can be classified into two types :

(*a*) *Intermolecular hydrogen bond.*

(*b*) *Intramolecular hydrogen bond.*

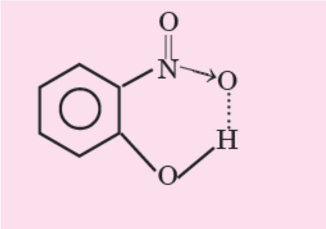
(*a*) Intermolecular hydrogen bond. Intermolecular hydrogen bond is formed between two different molecules of the same or different substances. For example,

(*i*) *hydrogen bond between the molecules of hydrogen fluoride.*

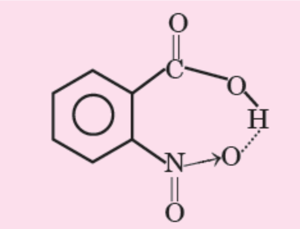
(*ii*) *hydrogen bond in alcohol or water molecules.*

Intermolecular hydrogen bond results into association of molecules. Hence, it usually increases the melting point, boiling point, viscosity, surface tension, solubility, etc.

(*b*) Intramolecular hydrogen bond. *Intramolecular hydrogen bond is formed between the hydrogen atom and the highly electronegative atom (F, O or N) present in the same molecule.* Intramolecular hydrogen bond results in the cyclisation of the molecules and prevents their association. Consequently, the effect of intramolecular hydrogen bond on the physical properties is negligible.



Ortho nitrophenol



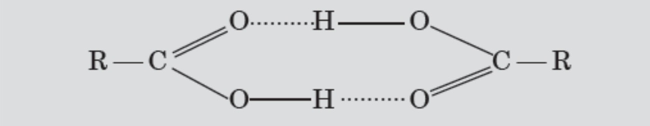
Ortho nitrobenzoic acid

For example, intramolecular hydrogen bonds are present in molecules such as *o*-nitrophenol, *o*-nitrobenzoic acid, etc.

Influence of Hydrogen Bonding on the Properties

Hydrogen bonding has important effect on many physical properties such as melting point, boiling point and solubility of the compounds. The main characteristics of compounds having hydrogen bonds are given below :

1.Association. Due to intermolecular hydrogen bonding, two or more molecules of a compound exist as associated molecules. For example, carboxylic acids (RCOOH) exist as dimers even in the vapour state as shown ahead :



This results in the increase in the size as well as in the molecular mass of the compound.

2. Higher melting and boiling points. The compounds containing hydrogen bonds have high melting and boiling points. It is due to the fact that because of hydrogen bonding, the electrostatic force of attraction in the molecules become large. Consequently, larger energy is required to separate these molecules before they can melt or boil. The influence of hydrogen bonding on melting and boiling points can be understood comparing the melting and boiling points of the hydrides of elements of groups 14, 15, 16 and 17 (Table 11).

Table 11. Melting and boiling points (K) of hydrides of groups 14, 15, 16 and 17.

Hydride	m.p.	b.p.
	Group 14	
CH_4	89.0	111.5
SiH_4	88.0	161.2
GeH_4	108.0	183.0
SnH_4	123.0	221.0
	Group 15	
NH_3	195.5	239.6
PH_3	138.0	185.0
AsH_3	159.0	218.0
SbH_3	184.0	256.0
	Group 16	
H_2O	273.0	373.0
H_2S	190.3	211.2
H_2Se	209.0	231.0
H_2Te	222.0	271.0
	Group 17	
HF	180.7	292.4
HCl	161.0	189.4
HBr	184.5	206.0
HI	222.2	237.0

The melting points and boiling points of hydrides of elements of these groups are also plotted against their molecular masses in Fig. 62(*a*) and 62(*b*). It is clear from Table 12. that the melting and boiling points increase as the molecular mass increases in group 14. This is mainly due to the fact that as the size of elements of group 14 increases, the number of electrons also increases. As a result, van der Waals' forces also increase and therefore, melting and boiling points increase. However, hydrides of groups 15, 16 and 17 do not show this trend. In these groups, the melting and boiling points also increase with increasing molecular mass with the exception of first member. But, the first members NH_3 (group 15), H_2O (group 16) and HF (group 17) have abnormally high melting and boiling points. The relatively high melting and boiling points of the first member of each group is due to the intermolecular hydrogen bonding shown by these compounds. For example, the boiling point of HF is much more than that of HCl due to larger hydrogen bonding in the former. Similarly, we can account for the higher values of boiling points of NH_3 and H_2O in their groups.

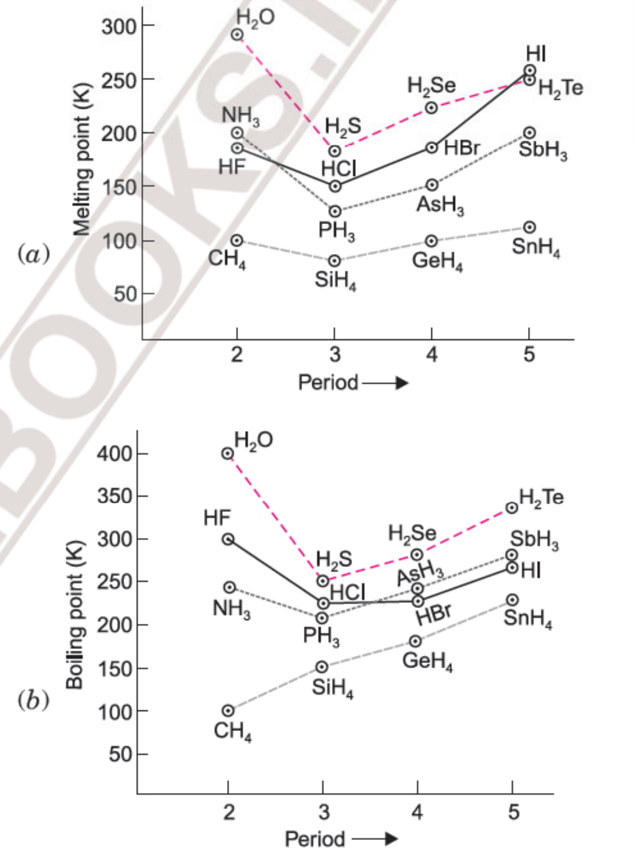


Fig. 62. (*a*) Melting points (*b*) Boiling points of hydrides of groups 14, 15, 16 and 17.

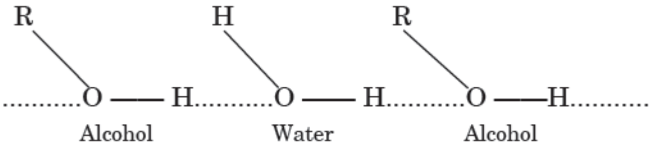
It is interesting to note that hydrogen bond in HF is stronger than in H_2O. However, water boils at a higher temperature than HF. This is due to the reason that each H_2O molecule is bonded to four other H_2O molecules (discussed later) through hydrogen bonds whereas each HF molecule is bonded to two other HF molecules through hydrogen bonds.

3. Influence on the physical state. Hydrogen bonding also influences the physical state of the substances (solid, liquid or gas). For example, both O and S belong to same group but H_2O is a liquid at ordinary temperature, while H_2S is a gas. This is explained on the basis of electronegativity values.

H_2O molecule	*H_2S molecule*
Electronegativity of O = 3.5	Electronegativity of S = 2.5
Electronegativity of H = 2.1	Electronegativity of H = 2.1

In water, oxygen is highly electronegative so that it forms hydrogen bonds. As a result, the molecules of H_2O get associated with one another and this raises the boiling point of water. Consequently, water exists as liquid at room temperature. On the other hand, the electronegativity difference of atoms in H_2S is less and hydrogen bonding in H_2S is almost negligible. As a result, H_2S is not associated and exists as a gas at room temperature.

4. Solubility. Hydrogen bonding also influences the solubility of one substance in another. For example, alcohol is highly soluble in water due to hydrogen bonding with water molecules as shown below :



5. Volatility. The compounds involving hydrogen bonding between different molecules such as NH_3, H_2O and HF have higher boiling points. Therefore, they are less volatile as compound to the other corresponding members of their groups. The enthalpies of vaporisation follows almost the same pattern as shown by their melting points and boiling points [Fig. 62(*a*) and (*b*)]. For example, in group 17, the enthalpies of vaporisation decrease in the order.

$HCl < HBr < HI < HF$

Similarly, in groups 15 and 16 the trends are :

$H_2S < H_2Se < H_2Te < H_2O$

$PH_3 < AsH_3 < SbH_3 < NH_3$

Practice Problems

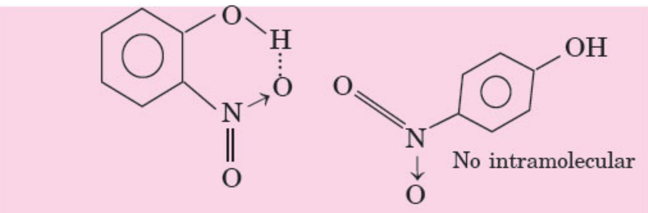
◑ **29.** Arrange the following in the decreasing order of their boiling points HF, HCl, HBr

◑ **30.** Do *o*-nitrophenol and *p*-nitrophenol have hydrogen bonding in their molecules? Explain which of the two has higher boiling point?

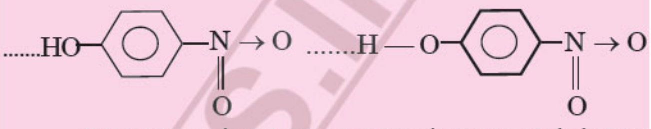
Answers to Practice Problems

◑ **29.** HF > HBr > HCl.

◑ **30.** Both have hydrogen bonding. *o*-Nitrophenol has **intramolecular** hydrogen bonds. But due to larger distance between —NO_2 and —OH groups in *p*-nitrophenol, there is no such bonding.



However, there is intermolecular hydrogen bonding in *p*-nitrophenol and therefore, it exists as associated molecule. In *o*-nitrophenol, no intermolecular hydrogen bonding is possible.



Due to associated nature of *p*-nitrophenol, it is less volatile and has high boiling point.

Water an unusual Liquid

Water is the most common substance on the earth's surface. It has many unusual properties. One of the most important of these is its ability to dissolve a variety of compounds. It dissolves many ionic compounds, many polar inorganic and organic compounds. In addition, water has high heat of vaporisation, high heat of fusion, high specific heat, good liquid range (from 0°C freezing point to 100°C boiling point).

Water has interesting structure and this accounts for its many unusual properties. These can be explained on the basis of hydrogen bonding.

Hydrogen bonding in water and ice

The phenomenon of hydrogen bonding is responsible for the interesting behaviour of water. It is a common observation that density of ice is less than that of water because ice always floats over water. Moreover, it is a well known fact that density of water is maximum at 4°C. Let us explain these observations :

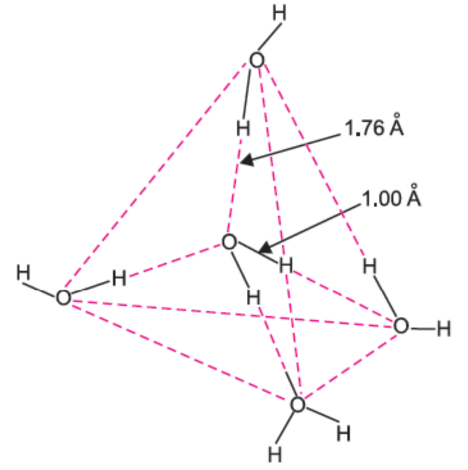


Fig. 63. Tetrahedral arrangement of water molecules.

(*i*) Ice is lighter than water.

X-ray studies have shown that in ice, each oxygen atom is tetrahedrally surrounded by four hydrogen atoms in such a way that two hydrogen atoms are linked to oxygen atom by covalent bonds. These hydrogen atoms lie closer to the oxygen atom at a distance of 1.00 Å. The other two hydrogen atoms are linked to the central oxygen atom by hydrogen bonds. They lie away from oxygen atom at a distance of 1.76Å. The oxygen atoms of water molecules are located at the corners of tetrahedron. This arrangement is shown in Fig. 64.

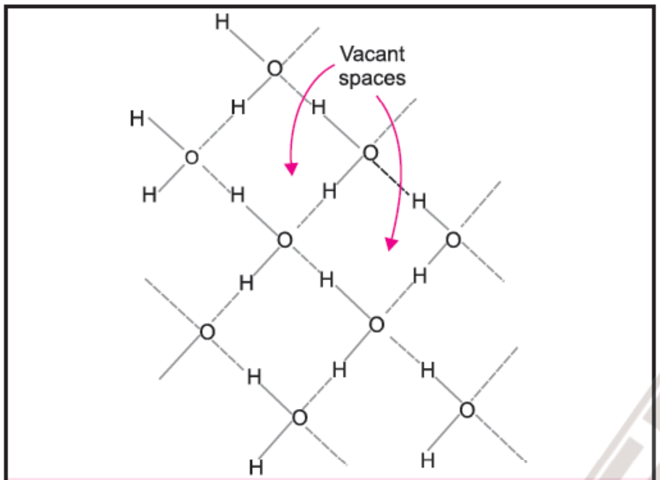


Fig. 64. Open cage like structure of ice.

As a result of tetrahedral arrangement of H_2O molecules in the solid state, the ice structure extends in three dimensions. Since hydrogen bonds between oxygen and H atoms are longer than the covalent bonds between them, the molecules of H_2O are not packed closely, but there are *vacant spaces* present in the crystal structure. This gives rise to an open cage like structure for ice having a larger volume for the given mass of water. Consequently, the density of ice is less than water.

(*ii*) Water has maximum density at 4°C.

When ice is melted by increasing its temperature, the open cage structure starts collapsing due to partial break down of the hydrogen bonds. This allows H_2O molecules to come closer and also the water molecules separated from ice structure fill the vacant spaces in open-cage structure. This results into concentration of volume. Hence, the density of water starts increasing on heating above the melting point of ice and becomes maximum at 4°C. On further rise in temperature, the kinetic energy of molecules increases and they once again start moving away from one another. This causes expansion which is much more than the concentration caused by breaking of hydrogen bonds. Therefore, above 4°C the density of water once again starts decreasing. Thus, the maximum density of water is at 4°C.

add on Conceptual Questions 3

CONCEPTUAL QA

Q. 1. In going from O_2 to O_2^+, the bond dissociation energy increases and bond length decreases. Do we expect the same behaviour for the change N_2 to N_2^+ ?

Ans. On going from $O_2 \longrightarrow O_2^+ + e^-$

bond order increases from 2 to 2.5 because the electron is lost from antibonding MO. Therefore, its bond dissociation energy increases but bond length decreases because bond order is directly proportional to bond dissociation energy but inversely proportional to bond length.

However, on going from

$$N_2 \longrightarrow N_2^+ + e^-$$

electron is lost from bonding MO and the bond order decreases from 3 to 2.5. Therefore, the bond dissociation energy decreases and the bond length increases.

Q. 2. Which of the two : O_2^- or O_2^{2-} has higher bond order and why ?

Ans. O_2^- has higher bond order (1.5) than O_2^{2-} (1.0) because O_2^- has lesser number of electrons in antibonding MOs.

Q. 3. Why is the energy of $\pi 2p_x$ and $\pi 2p_y$ MOs lower than $\sigma 2p_z$ MO in N_2 molecule ?

Ans. This is because of intermixing of 2*s* and $2p_z$ orbitals because of their close proximity. Due to intermixing $\sigma 2p_z$ MO becomes higher in energy than $\pi 2p_x$ and $\pi 2p_y$ MOs.

Q. 4. Write which one out of O_2^+ and O_2^- is more stable on the basis of bond order calculations.

Ans. Bond order in O_2^+ is 2.5 and in O_2^- is 1.5. Therefore, O_2^+ is more stable.

Q. 5. Use molecular orbital theory to explain why the Be_2 molecule does not exist. *N.C.E.R.T.*

Ans. M.O. energy level configuration for Be_2 molecule is

Be_2 : KK $(\sigma 2s)^2 (\sigma^* 2s)^2$ Bond order = $\frac{2-2}{2} = 0$

Since bond order of Be_2 molecule is zero, this means that Be_2 molecule does not exist.

Q. 6. Compare the relative stability of the following species and indicate their magnetic properties: O_2, O_2^+, O_2^- (superoxide), O_2^{2-}(peroxide). *N.C.E.R.T.*

Ans. The stability can be decided on the basis of bond order as :

O_2 : KK $(\sigma 2s)^2(\sigma 2s^*)^2(\sigma 2p_z)^2(\pi 2p_x)^2(\pi 2p_y)^2(\pi^* 2p_x)^1(\pi^* 2p_y)^1$	Bond order = $\frac{8-4}{2} = 2$	Paramagnetic
O_2^+ : KK $(\sigma 2s)^2(\sigma 2s^*)^2(\sigma 2p_z)^2(\pi 2p_x)^2(\pi 2p_y)^2(\pi^* 2p_x)^1$	Bond order = $\frac{8-3}{2} = 2.5$	Paramagnetic
O_2^- : KK $(\sigma 2s)^2(\sigma 2s^*)^2(\sigma 2p_z)^2(\pi 2p_x)^2(\pi 2p_y)^2(\pi^* 2p_x)^2(\pi^* 2p_y)^1$	Bond order = $\frac{8-5}{2} = 1.5$	Paramagnetic
O_2^{2-} : KK $(\sigma 2s)^2(\sigma 2s^*)^2(\sigma 2p_z)^2(\pi 2p_x)^2(\pi 2p_y)^2(\pi^* 2p_x)^2(\pi^* 2p_y)^2$	Bond order = $\frac{8-6}{2} = 1$	Diamagnetic

Larger the bond order greater is the stability, So the stability decreases as : $O_2^+ > O_2 > O_2^- > O_2^{2-}$

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

(a) $N_2 \longrightarrow N_2^+ + e^-$ **(b)** $O_2 \longrightarrow O_2^+ + e^-$

Ans. (*a*) Bond order decreases from 3 to 2.5

(*b*) Bond order increases from 2 to 2.5

Q. 8. List two main conditions for forming hydrogen bonds.

Ans. (*i*) High electronegativity of atom bonded to hydrogen.

(*ii*) Small size of the electronegative atom.

Q. 9. Why does formic acid exist as dimer ? What is its one consequence ?

Ans. Formic acid exists as dimer because of hydrogen bonding.

Because of hydrogen bonding, it has larger size as well as molecular mass.

Q. 10. Select the molecule in each of the following having higher property mentioned :

(*i*) F ....H–F, F–H........O : stronger hydrogen bond
(*ii*) CH_4, SiH_4 : boiling point
(*iii*) HF, HCl : boiling point
(*iv*) Ice, water : density

Ans. (*i*) F........H–F (*ii*) SiH_4 (*iii*) HF (*iv*) water.

Q. 11. How can one non-polar molecule induce a dipole in a nearby non-polar molecule ? *N.C.E.R.T.*

Ans. In a non-polar molecule, there may be instantaneous dipole created by specific positions of electrons. This instantaneous dipole can induce a dipole in a nearby non-polar molecule.

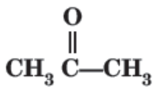
Q. 12. Considering *z*-axis as the internuclear axis, which of the following will not form sigma bond ?

(*a*) 2*s* and 2*s* **(*b*)** $2p_y$ and $2p_y$ **(*c*)** 2*s* and $2p_z$ **(*d*)** $2p_x$ and $2p_z$ **(*e*)** $2p_z$ and $2p_z$.

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

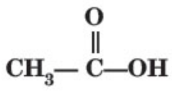
Q. 13. Which of the following substances exhibit hydrogen bonding? Draw the hydrogen bonds between two molecules of the substance where appropriate :

(*i*) CH_3CH_2OH (*ii*)



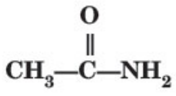
$CH_3\overset{\overset{O}{\|}}{C}-CH_3$

(*iii*)



$CH_3-\overset{\overset{O}{\|}}{C}-OH$

(*iv*)

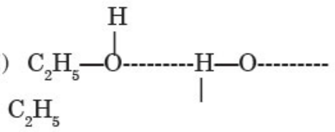


$CH_3-\overset{\overset{O}{\|}}{C}-NH_2$

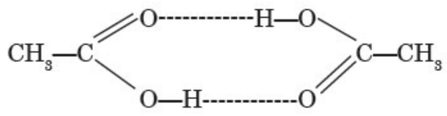
N.C.E.R.T.

Ans. (*i*), (*iii*) and (*iv*) exhibit hydrogen bonding.

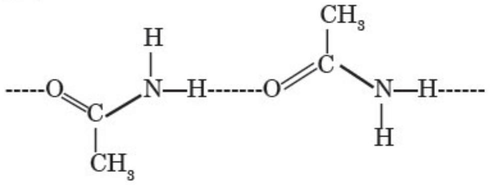
(*i*)



(*iii*)



(*iv*)



Chapter Summary

Key Terms

- **Chemical bond.** The attractive force which holds together the constituent particles (atoms, ions or molecules) in a chemical specie.
- **Ionic bond or electrovalent bond.** The electrostatic force which holds the oppositely charged ions together.
- **Electrovalency.** The number of electrons which an atom loses or gains.
- **Covalent bond.** The bond formed by mutual sharing of electrons between combining atoms of the same or different elements.
- **Coordinate bond.** A covalent bond in which both the electrons in the shared pair come from one atom.
- **Lattice enthalpy.** The amount of energy released when one mole of ionic crystal is formed from its constituent ions in gaseous state.
- **Dipole moment.** A vector quantity defined as the product of charge developed on any of the atom in a bond and distance between the atoms.
- **Hybridisation.** The phenomenon of intermixing of the orbitals of slightly different energies so as to redistribute their energies and to give new set of orbitals of equivalent energies and shape.
- **Resonance.** When a molecule cannot be represented by a single structure but its characteristic properties can be described by two or more than two structures, then the actual structure is said to be resonance hybrid of these structures. This phenomenon is called **resonance.** The various contributing structures are called **resonating structures.**
- **Canonical form.** The contributing structures taken together contribute the resonance hybrid which represents the molecule or ion.
- **Resonance energy.** The difference between the actual bond energy and the most stable of the resonating structures.

QUICK CHAPTER ROUND UP

CHEMICAL BONDS

Ionic Bond
formed by transfer of electrons from one atom to other

- The ionisation enthalpy of atom forming the cation should be low.
- The electron gain enthalpy of atom forming the anion should be highly negative.
- Lattice enthalpy should be high.

Covalent Bond
formed by sharing of electrons between atoms

- Each atom may contribute one or more electrons for sharing
- Atoms attain stable noble gas configurations.

Coordinate Bond
covalent bond in which both the electrons in the shared pair come from one atom.

- One of the atoms or group of atoms is deficient of two electrons
- Other atom has stable noble gas configuration

Lattice Enthalpy depends upon
- **Size of ions.** Smaller the size of ion, higher is lattice enthalpy
- **Charge on ions.** Greater the charge on ions, higher is lattice enthalpy

➤ LiF > NaF > KF > RbF ; $AlCl_3 > BaCl_2 > NaCl$

Exceptions to Octet rule
- Incomplete octet

H : Be : H , $\overset{F}{\ddot{\text{F : B : F}}}$

- Expanded octet

PF_5, SF_6, IF_7
- Odd electron molecules

Nitric oxide   Nitrogen dioxide

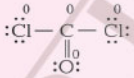
FORMAL CHARGE

Formal charge on an atom =

$$\begin{pmatrix}\text{Total number of}\\ \text{valence electrons}\\ \text{in free atom}\end{pmatrix} - \begin{pmatrix}\text{Total number of}\\ \text{non-bonding}\\ \text{(lone pair) electrons}\end{pmatrix} - \frac{1}{2}\begin{pmatrix}\text{Total number of}\\ \text{bonding}\\ \text{(shared) electrons}\end{pmatrix}$$

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

e.g.,



RESONANCE STRUCTURES

Dipole Moment

The product of the magnitude of the charge and the distance of separation between the charges

$\mu = q \times d$

Units: **Debye**

1D = 1×10^{-18} esu.cm

% Ionic character =

$$\frac{\text{Observed dipole moment}}{\text{Dipole moment for complete ionic character}} \times 100$$

➤ If electronegativity difference (ΔEN) is 1.7

⇒ 50% ionic & 50% covalent

ΔEN > 1.7 ⇒ ionic

ΔEN < 1.7 ⇒ covalent

Symmetrical molecules ⇒ Non-polar

CO_2 , BF_3, BeF_2, CH_4

Unsymmetrical molecules ⇒ Polar

H_2O , NH_3, $CHCl_3$

NH_3 ⇒ 1.47 D

NF_3 ⇒ 0.24D

- Fajan's rules

  Covalent character will be favoured by
  - (*i*) Small size of cation
  - (*ii*) Large size of anion
  - (*iii*) High charge of cation and anion
  - (*iv*) The cation having 18-electrons shell.

According to **quantum theory of covalent bond**, *the bond is formed by the overlapping of half filled atomic orbitals having electrons with opposite spins. The greater the overlapping, the stronger is the bond formed between two atoms.*

The relative arrangement of the bonded atoms in a molecule is called **geometry of the molecule**.

VSEPR THEORY

helps to predict the shapes/geometries of molecules. Shapes are predicted from number of electron pairs

Lone pair-Lone pair > Lone pair-Bond pair > Bond pair-Bond pair.

Molecules with bond pairs only

2 bond pairs ⇒ Linear

e.g., $BeCl_2$, CO_2

4 bond pairs ⇒ Tetrahedral

e.g., CH_4, SiF_4

6 Bond pairs ⇒ Octahedral

e.g., SF_6, TeF_6

3 Bond pairs ⇒ trigonal planar

e.g., BF_3, $AlCl_3$

5 Bond pairs ⇒ trigonal bipyramidal

e.g., PF_5, $SbCl_5$

7 Bond pairs ⇒ pentagonal bipyramidal

e.g., IF_7

Molecules with bond pairs and lone pairs

AB_3L

NH_3 ⇒ pyramidal

AB_4L

SF_4 ⇒ See saw

AB_5L

BrF_5 ⇒ Square pyramidal

AB_2L_2

Water ⇒ V-shaped

AB_3L_2

ClF_3 ⇒ T shaped

AB_4L_2

XeF_4 ⇒ Square planar

AB_2L_3

XeF_2 ⇒ Linear

The hybridisation also helps to know the geometry of molecules.

MOLECULAR ORBITAL THEORY

- MOs are formed by the combination of atomic orbitals of same symmetry and of nearly same energy.
- If *z*-axis is internuclear axis, $2p_z$ orbitals combine to form σ MOs while $2p_x$ and $2p_y$ can combine to form π MOs.
- 2s orbital may combine with $2p_z$ orbital but it cannot combine with $2p_x$ or $2p_y$ orbitals.
- Larger the bond order of a molecule, greater will be its bond dissociation energy and smaller will be its bond length.

Sequence of energy levels
- For molecules Li_2, Be_2, B_2, C_2, N_2

  $\sigma 1s, \sigma^* 1s, \sigma 2s, \sigma^* 2s,\ \pi 2p_X = \pi 2p_y, \sigma 2p_Z, \pi^* 2p_X = \pi^* 2p_y, \sigma^* 2p_Z$
- For molecules O_2, F_2, Ne_2

  $\sigma 1s, \sigma^* 1s, \sigma 2s, \sigma^* 2s, \sigma 2p_Z, \pi 2p_X = \pi 2p_y, \pi^* 2p_X = \pi^* 2p_y,\ \sigma^*\ 2p_Z$

Bond order

$$= \frac{\begin{bmatrix}\text{No. of electrons}\\ \text{in bonding MOs}\end{bmatrix} - \begin{bmatrix}\text{No. of electrons}\\ \text{in anti-bonding MOs}\end{bmatrix}}{2}$$

- Larger the B.O., smaller the bond length
- Larger the B.O., greater the bond dissociation energy

⇒

For O_2, O_2^+, O_2^-, O_2^{2-}

Bond order

O_2^+ (2.5) > O_2(2) > O_2^- (1.5) > O_2^{2-} (1)

Bond length

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

Bond dissociation energy

$O_2^+ > O_2 > O_2^- > O_2^{2-}$

Paramagnetic species ⇒ O_2, O_2^+, O_2^-

B_2 molecule is paramagnetic because of its MO electronic configuration : KK $(\sigma 2s)^2$ $(\sigma^* 2s)^2$ $(\pi 2p_x)^1$ $(\pi 2p_y)^1$. In this case $\pi 2p_x$ and $\pi 2p_y$ MOs have lower energy than $\sigma 2p_z$ MO.

➤ Intermolecular H-bond formed between two different molecules.

➤ Intramolecular H-bond formed between H atom and electronegative atom in the same molecule.

Because of H-bonding

- Molecules have higher mpt and bpt.
- exist as associated
- Ice floats over water.

NCERT FILE *Solved*

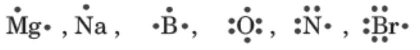
NCERT Textbook Exercises

Q. 1. Explain the formation of a chemical bond.

Ans. *Refer Text page 1, 2.*

Q. 2. Write Lewis dot symbols for atoms of the following elements : Mg, Na, B, O, N, Br.

Ans.



Q. 3 Write Lewis symbols for the following atoms and ions :

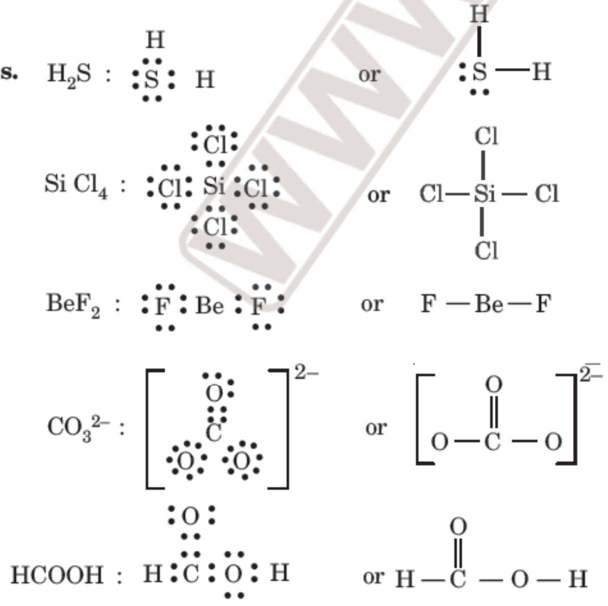
S and S^{2-}; Al and Al^{3+}; H and H^-

Ans. *Refer Solved Example 2. (Page 3)*

Q. 4 Draw the Lewis structures for the following molecules and ions :

H_2S, $SiCl_4$, BeF_2, CO_3^{2-}, HCOOH

Ans.



Q. 5. Define octet rule. Write its significance and limitations.

Ans. Atoms combine either by transfer of valence electrons from one atom to another (gaining or losing) or by sharing of valence electrons in order to complete their octets in their valence shell. This is called the octet rule.

Significance : The octet rule helps to explain as to why different atoms combine with each other to form ionic or covalent compounds.

Limitations of octet rule. *Refer exceptions to the octet rule (Page 13).*

Q. 6. Write the favourable factors for the formation of ionic bond.

Ans. The favourable factors for the formation of ionic bonds are :

(*i*) Low ionization enthalpy of the metal atom.

(*ii*) High electron gain enthalpy of the non-metal atom.

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

Q. 7. Discuss the shape of the following molecules using the VSEPR model :

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

Ans. *Refer Text (Page 28, 29).*

Q. 8. 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 molecule has one lone pair while H_2O has two lone pairs of electrons. Due to the presence of lone pairs the geometries of NH_3 and H_2O are distorted. Due to the presence of stronger *lp–bp* repulsion than *bp–bp* repulsion, the bond angle in NH_3 is reduced from normal tetrahedral bond angle (109.5°) to 107°. In case of H_2O, two *lp* of electrons force the O—H bonds more closely than N–H bonds in NH_3. So the bond angle decreases to a larger extent *i.e.*, to 104.5°.

Q. 9. How do you express the bond length in terms of bond order ?

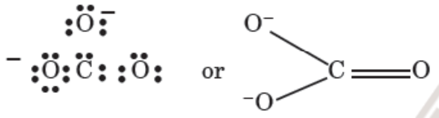
Ans. Greater the bond order, smaller is the bond length.

Q. 10. Define bond length.

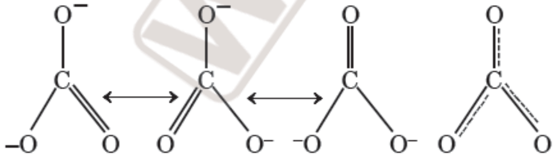
Ans. Bond length is defined as the average distance between the centres of the nuclei of two bonded atoms in a molecule. In other words, it represents the equilibrium internuclear separation distance of the bonded atoms in a molecule.

Q. 11. Explain the important aspects of resonance with reference to the CO_3^{2-} ion.

Ans. When a molecule cannot be represented by a single structure but its characteristic properties can be described by two or more than two structures, then the actual structure is said to be a resonance hybrid of these structures. For example, the carbonate ion may be represented as :

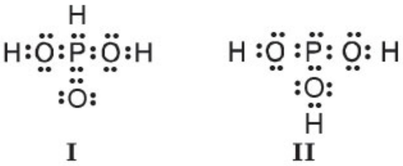


In this case, each atom has an octet of electrons. According to this structure, there are single bonds between two carbon—oxygen atoms and one double bond between carbon and oxygen atoms. Therefore, the two C—O bonds should be different than the third C═O bond. However, experimentally, it is observed that all the three bond lengths are equal and the bonds are intermediate between single and double bonds. This means that the above Lewis structure does not account for the observed experimental facts. To solve the problem, the CO_3^{2-} may be represented as resonance hybrid of the following structures.



Resonance hybrid

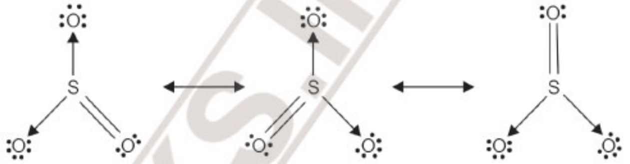
Q. 12. H_3PO_3 can be represented by structures 1 and II shown below. Can these two structures be taken as the canonical forms of the resonance hybrid representing H_3PO_3 ? If not, give reasons for the same.

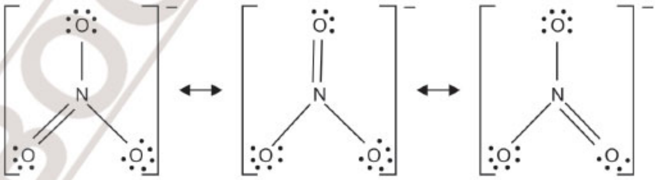


Ans. No, these cannot be taken as canonical forms because the position of atoms have changed.

Q. 13. Write the resonance structures for SO_3, NO_2 and NO_3^-.

Ans.





Q. 14. 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. *Refer Solved Example 4.(Page 7)*

Q. 15. 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. CO_2 has zero dipole moment. This means that CO_2 molecule is linear so that the two C = O bond moments get cancelled giving zero resultant dipole moment. However, H_2O molecule has resultant dipole moment showing that it cannot be linear.The two O–H bonds are arranged in angular shape and the bond moment of two O–H bonds give resultant dipole moment.

Q. 16. Write the significance/applications of dipole moment.

Ans. *Refer Text (Page 24).*

Q. 17. Define electronegativity. How does it differ from electron gain enthalpy ?

Ans. *Refer unit 3.*

Q. 18. Explain with the help of suitable example polar covalent bond.

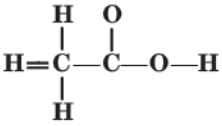
Ans. The bond formed between atoms having different electronegativities is called polar covalent bond. Greater the difference in the electronegativities of the atoms forming the bond, greater will be the polarity of the molecule. For example, the following bonds are polar covalent bonds :

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

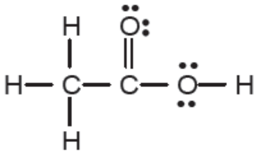
Q. 19. Arrange the bonds in order of increasing ionic character in the molecules : LiF, K_2O, N_2, SO_2 and ClF_3.

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

Q. 20. The skeletal structure of CH_3COOH as shown below is correct, but some of the bonds are shown incorreectly. Write the correct Lewis structure for acetic acid.



Ans. Correct Lewis structure of CH_3COOH is



Q. 21. 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. In square planar geometry, the bond angle will be 90° which is less than bond angle in tetrahedral geometry (109.5°). Therefore, repulsive forces between electron pairs will be more in square planar geometry and it will be less stable in comparison to tetrahedral geometry.

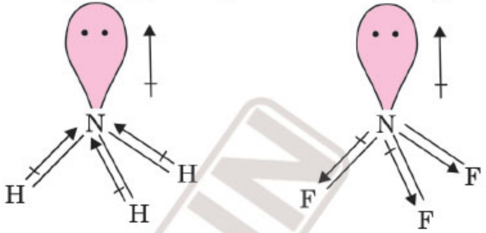
Q. 22. Explain why BeH_2 molecule has a zero dipole moment although, the Be—H bonds are polar.

Ans. BeH_2 molecule is linear molecule, therefore, the resultant dipole moment of two Be–H bonds get cancelled giving zero dipole moment.

$$H \leftarrow\!\!+ Be +\!\!\rightarrow H \quad \mu = 0$$

Q. 23. Which out of NH_3 and NF_3 has higher dipole moment and why ?

Ans. NH_3 has higher dipole moment than NF_3. Both NH_3 and NF_3 molecules have pyramidal shape with one lone pair on nitrogen atom. Fluorine is more electronegative that hydrogen and therefore, the N—F bonds should be more polar than N—H bonds. Consequently, the resultant dipole moment of NF_3 should be much larger than that of NH_3. However, the dipole moment of ammonia ($\mu = 1.47$ D) is larger than that of NF_3 ($\mu = 0.24$ D). This is due to the presence of lone pair on nitrogen. In case of NH_3, the orbital dipole due to lone pair is in the same direction as the resultant dipole moment of the three N—H bonds. Therefore, it adds on the resultant dipole moment of the N—H bonds. On the other hand, in case of NF_3, the orbital dipole is in the opposite direction to the resultant dipole moment of the three N—F bonds. Thus, the lone pair moments cancel the resultant N—F bond moments as shown in figure. Consequently, the dipole moment of NF_3 is low.



Q. 24. What is meant by hybridisation of atomic orbitals? Describe the shapes of *sp*, *sp*², *sp*³ hybrid orbitals.

Ans. *Refer Text (Page 40-42).*

Q. 25. Describe the change in hybridisation (if any) of the Al atom in the following reaction :

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

Ans. It changes from sp^2 (in $AlCl_3$) to sp^3 in $AlCl_4^-$.

Q. 26. Is there any change in the hybridisation of B and N atoms as a result of the following reaction ?

$$BF_3 + NH_3 \longrightarrow F_3B.NH_3$$

Ans. *Refer Solved Example 14. (Page 48)*

Q. 27. 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. *Refer Text (Page 44–45).*

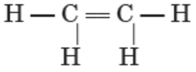
Q. 28. What is the total number of sigma and pi bonds in the following molecules ?

(*a*) C_2H_2 $\qquad$ **(*b*) C_2H_4**

Ans. (*i*) $H—C\equiv C—H$ $\qquad$ σ bonds = 3

π bonds = 2

(*ii*)



$$H—\underset{\displaystyle H}{\underset{|}{C}}=\underset{\displaystyle H}{\underset{|}{C}}—H$$

σ bonds = 5

π bonds = 1

Q. 29. Considering x-axis as the internuclear axis which out of the following will not form a sigma bond and why ? (*a*) 1*s* and 1*s* (*b*) 1*s* and 2p_x (c) 2p_y and 2p_y (d) 1*s* and 2*s*.

Ans. Only (c) will not form a σ bond because taking x-axis as the internuclear axis, there will be sidewise overlap between the two 2p_y orbitals forming a π-bond. All others will form σ-bond.

Q. 30. Which hybrid orbitals are used by carbon atoms in the following molecules ?

(*a*) $CH_3 — CH_3$ $\qquad$ **(*b*) $CH_3—CH=CH_2$**

(*c*) $CH_3—CH_2—OH$ $\qquad$ **(*d*) $CH_3—CHO$**

(*e*) CH_3COOH

Ans. *Refer Solved Example 13. (Page 48)*

Q. 31. What do you understand by bond pairs and lone pairs of electrons ? Illustrate by giving one example of each type.

Ans. *Refer Text (Page 27–28).*

Q. 32. Distinguish between a sigma and a pi bond.

Ans. *Refer Table 9, (Page 37).*

Q. 33. Explain the formation of H_2 molecule on the basis of valence bond theory.

Ans. *Refer Text (Page 35-36).*

Q. 34. Write the important conditions required for the linear combination of atomic orbitals to form molecular orbitals.

Ans. *Refer Text (Page 52).*

Q. 35. Use molecular orbital theory to explain why the Be_2 molecule does not exist.

Ans. M.O. electronic configuration of Be_2 molecule is

$Be_2 : KK\,(\sigma 2s)^2\,(\sigma^* 2s)^2$

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

Since bond order of Be_2 molecule is zero, therefore, Be_2 molecule does not exist.

Q. 36. 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. *Refer Conceptual Questions [3], Q.6 (Page 69).*

Q. 37. Write the significance of a plus and a minus sign shown in representing the orbitals.

Ans. Plus and minus sign corresponds to sign of electron wave. The crests of a wave are usually given +ve sign and troughs of a wave are given –ve sign.

Q. 38. Describe the hybridisation in case of PCl_5. Why are the axial bonds longer as compared to equatorial bonds?

Ans. *Refer Text (Page 29).*

Q. 39. Define hydrogen bond. Is it weaker or stronger than the van der Waals forces?

Ans. The attractive force which binds hydrogen atom of one molecule with electronegative atom (F, O or N) of another molecule is called hydrogen bond. Hydrogen bond is stronger than the van der Waals forces of attraction.

Q. 40. What is meant by the term bond order? Calculate the bond order of : N_2, O_2, O^+_2 and O^-_2.

Ans. Bond order is defined as the number of covalent bonds in a covalent molecule. It is equal to one half of the difference between the number of electrons in the bonding and antibonding molecular orbitals i.e.

$$\text{Bond order} = \frac{\text{No. of electrons in bonding M.Os.} - \text{No. of electrons in anti bonding M.Os.}}{2}$$

$N_2 : KK\,(\sigma 2s)^2\,(\sigma^* 2s)^2\,(\pi 2p_x)^2\,(\pi 2p_y)^2\,(\sigma 2p_z)^2$

$$B.O = \frac{8-2}{2} = 3$$

$O_2 : KK\,(\sigma 2s)^2\,(\sigma^* 2s)^2\,(\sigma 2p_z)^2\,(\pi 2p_x)^2(\pi 2p_y)^2\,(\pi^* 2p_x)^1\,(\pi^* 2p_y)^1$

$$B.O = \frac{8-4}{2} = 2$$

$O_2^+ : KK\,(\sigma 2s)^2\,(\sigma^* 2s)^2\,(\sigma 2p_z)^2\,(\pi 2p_x)^2\,(\pi 2p_y)^2\,(\pi^* 2p_x)^1$

$$B.O = \frac{8-3}{2} = 2.5$$

$O_2^- : KK\,(\sigma 2s)^2\,(\sigma^* 2s)^2\,(\sigma 2p_z)^2\,(\pi 2p_x)^2(\pi 2p_y)^2\,(\pi^* 2p_x)^2\,(\pi^* 2p_y)^1$

$$B.O = \frac{8-5}{2} = 1.5$$

NCERT Exemplar Problems

Note: *Objective Questions from Exemplar Problems are given in Competition File, page 104*

Short Answer Questions *Carrying 2 or 3 marks*

Q. 1. Explain the non-linear shape of H_2S and non-planar shape of PCl_3 using valence shell electron pair repulsion theory.

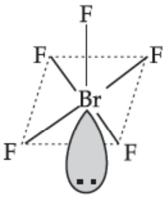
Ans. *Refer Text (Page 31;* similar to H_2O and NH_3).

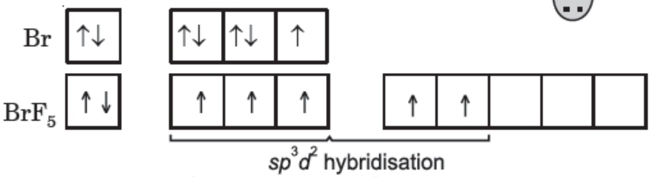
Q. 2. Using molecular orbital theory, compare the bond energy and magnetic character of O_2^+ and O_2^- species.

Ans. *Refer Text (Page 61-62).*

Q. 3. Explain the shape of BrF_5.

Ans. BrF_5 involves sp^3d^2 hybridisation and has one lone pair of electrons as :

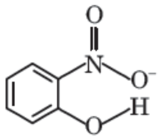




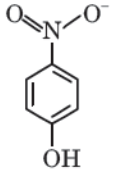
The shape is square pyramidal.

Subjective Questions

Q. 4. Structures of molecules of two compounds are given below :



(I)



(II)

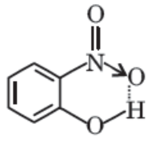
(*a*) Which of the two compounds will have intermolecular hydrogen bonding and which compound is expected to show intramolecular hydrogen bonding ?

(*b*) Which of the above two compounds will show higher melting point?

(*c*) Which of the above compounds will form hydrogen bond with water easily and be more soluble in it?

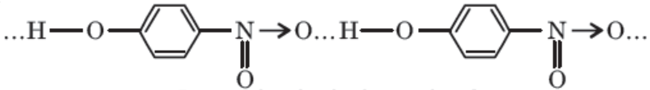
Ans. (*a*) Compound I will form intramolecular hydrogen bonding because NO_2 and OH groups are close together.

Compound II will form intermolecular hydrogen bonding.



I

Intramolecular hydrogen bond



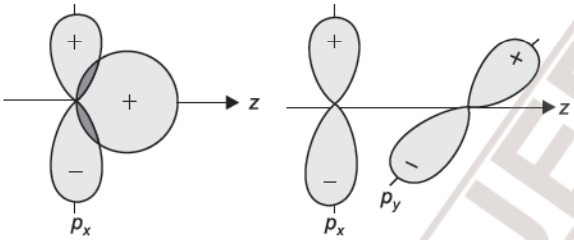
Intermolecular hydrogen bond

II

(*b*) Compound II will have higher melting point because during intermolecular hydrogen bond, more and more molecules are joined together through hydrogen bond formation.

(*c*) Because of intramolecular hydrogen bonding compound I will not be able to form hydrogen bonds with water. Therefore, compound I will be less soluble in water. On the other hand, compound II can form hydrogen bonds with water more easily and therefore, will be soluble in water.

Q. 5. Why does type of overlap given in the following figure not result in bond formation ?



Ans. In first figure, the ++ overlap is equal to + – overlap and therefore, these cancel out and net overlap is zero.

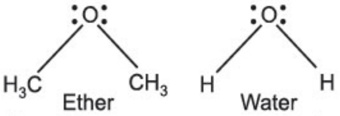
In second figure, no overlap is possible because the two orbitals are perpendicular to each other.

Q. 6. Explain why PCl_5 is trigonal bipyramidal whereas IF_5 is square pyramidal.

Ans. *Refer Text (Pages 29 and 33).*

Q. 7. In both water and dimethyl ether (CH_3—O—CH_3), oxygen atom is central atom, and has the same hybridisation, yet they have different bond angles. Which one has greater bond angle ? Give reason.

Ans. Dimethyl ether has larger bond angle than water. This is because there is more repulsion between bond pairs of CH_3 groups attached in ether than between bond pairs of hydrogen atoms attached to oxygen in water. The carbon of CH_3 group in ether is attached to three hydrogen atoms through σ bonds and electron pairs of these bonds add to the electron charge density on carbon atom. Hence, repulsion between two—CH_3 groups will be more than that between two H atoms.



Q. 8. Write Lewis structure of the following compounds and show formal charge on each atom.

HNO_3, NO_2, H_2SO_4.

Ans. *Refer Text (Pages 10-11).*

Q. 9. Write the complete sequence of energy levels in the increasing order of energy in the molecule. Compare the relative stability and the magnetic behaviour of the following species :

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

Ans. *Refer Text (Page 61).*

Q. 10. What is the effect of the following processes on the bond order of N_2 and O_2 ?

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

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

Ans. (*a*) Bond order decreases from 3 to 2.5

(*b*) Bond order increases from 2 to 2.5

Q. 11. Give reasons for the following :

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

(*ii*) Water molecule has bent structure whereas carbon dioxide molecule is linear.

(*iii*) Ethyne molecule is linear.

Ans. *Refer Text.*

Q. 12. What is an ionic bond ? With two suitable examples explain the difference between an ionic and a covalent bond ?

Ans. *Refer Text.*

Q. 13. Arrange the following bonds in order of increasing ionic character giving reason.

N—H, F—H, C—H and O—H.

Ans. Electronegativity difference

N—H	F—H	C—H	O—H
3.0 − 2.1	4.0 − 2.1	2.5 − 2.1	3.5 − 2.1
= 0.9	= 1.19	= 0.4	= 1.4

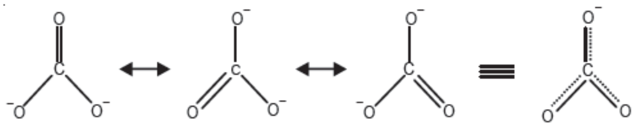
Increasing order of electronegativity difference :

C – H < N – H < O – H < F – H

Greater is the difference in electronegativity between two bonded atoms, greater is the ionic character.

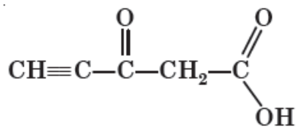
Q. 14. Explain why CO_3^{2-} ion cannot be represented by a single Lewis structure. How can it be best represented ?

Ans. A single structure of carbonate cannot explain all the properties of the ions. It can be represented as resonance hybrid of the following structures :

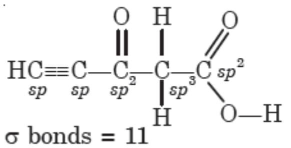


According to a single structure, there are two types of bonds one double C = O and two single C – O bonds. But actually all the bonds are identical with same bond length and bond strength. This can be explained by resonance.

Q. 15. Predict the hybridisation of each carbon in the molecule of organic compound given below. Also indicate the total number of sigma and pi bonds in this molecule.



$CH\equiv C-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{O}{/\!/}}{C}-OH$

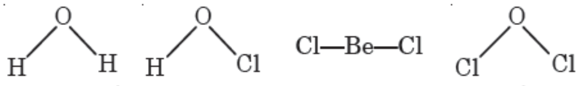
Ans. 

σ bonds = 11

π bonds = 4

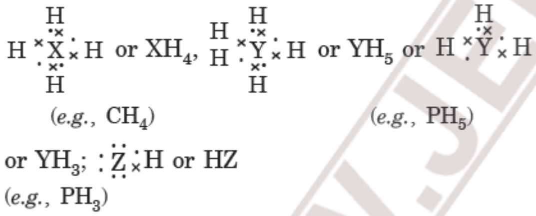
Q. 16. Group the following as linear and non-linear molecules :

H_2O, HOCl, $BeCl_2$, Cl_2O.

Ans. 

Non–linear Linear Non–linear

Q. 17. Elements X, Y and Z have 4, 5 and 7 valence electrons respectively. (*i*) Write the molecular formula of the compounds formed by these elements individually with hydrogen. (*ii*) Which of these compounds will have the highest dipole moment ?

Ans. (*i*) 

H ×X× H or XH_4, H ×Y× H or YH_5 or H Y H

(*e.g.*, CH_4) (*e.g.*, PH_5)

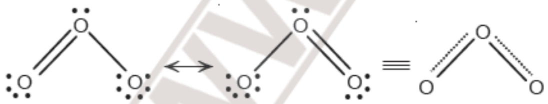
or YH_3; :Z×H or HZ

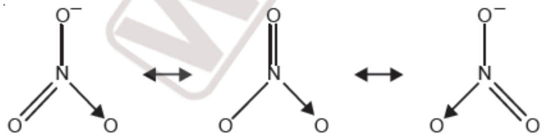
(*e.g.*, PH_3)

(*ii*) Z will be most electronegative element and hence HZ will have highest dipole moment.

Q. 18. Draw the resonating structure of

(*i*) Ozone molecule (*ii*) Nitrate ion.

Ans. (*i*) 

(*ii*) 

Q. 19. Predict the shapes of the following molecules on the basis of hybridisation.

BCl_3, CH_4, CO_2, NH_3.

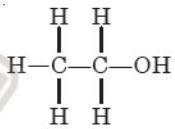
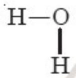
Ans. *Refer Text (Page 41–43).*

Q. 20. All the C—O bonds in carbonate ion (CO_3^{2-}) are equal in length. Explain.

Ans. On the basis of resonance. *Refer Text* and *NCERT Exemplar Problem Q. 14.*

Q. 21. What is meant by the term average bond enthalpy ? Why is there difference in bond enthalpy of O—H bond in ethanol (C_2H_5OH) and water ?

Ans. The average of the bond dissociation enthalpies of different bonds in polyatomic molecules (which contain more than one bond of the same type) is called average bond enthalpy.

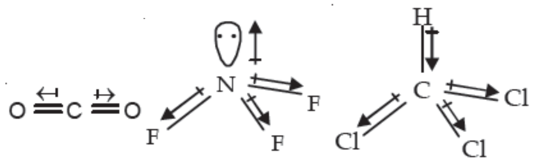
The O—H bonds in ethanol,  and water  donot have similar environment around oxygen atom. Hence, their O—H bond enthalpies are different.

Long Answer Questions *Carrying 5 marks*

Q. 22. (*i*) Discuss the significance/applications of dipole moment.

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

Ans. (*i*) *Refer Text (Page 24).*

(*ii*) 

μ = 0 μ = 0.24D μ = 1.02D

Q. 23. Use the molecular orbital energy level diagram to show that N_2 would be expected to have a triple bond, F_2, a single bond and Ne_2, no bond.

Ans. *Refer Text (Page 61).*

Q. 24. Briefly describe the valence bond theory of covalent bond formation by taking an example of hydrogen. How can you interpret energy changes taking place in the formation of dihydrogen ?

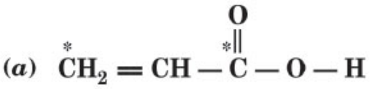
Ans. *Refer Text (Page 35).*

Q. 25. Describe hybridisation in the case of PCl_5 and SF_6. The axial bonds are longer as compared to equatorial bonds in PCl_5 whereas in SF_6 both axial bonds and equatorial bonds have the same bond length. Explain.

Ans. *Refer Text.*

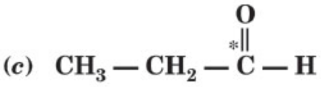
Q. 26. (*i*) Discuss the concept of hybridisation. What are its different types in a carbon atom.

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



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

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



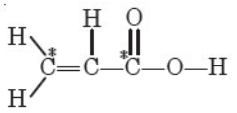
(c) $CH_3-CH_2-\overset{O}{\overset{\|}{\overset{*}{C}}}-H$

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

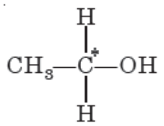
(e) $CH_3-\overset{*}{C}\equiv CH$

Ans. (*i*) *Refer Text (Page 36).*

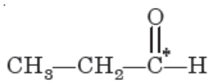
(*ii*) (*a*)



sp^2, sp^2

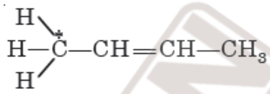


(*b*) $CH_3-\underset{H}{\overset{H}{\overset{*}{C}}}-OH$ sp^3



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

(*d*)



sp^3

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

QUICK MEMORY TEST

A. Say True or False

1. Ionic compounds are bad conductors of electricity in the solid state.
2. The shape of SF_6 molecule is octahedral whereas that of IF_7 is square pyramidal.
3. The bond order of CO molecule is 2.5.
4. As N—F bond is more polar than N—H bond, NF_3 molecule has higher dipole moment than NH_3.
5. The bond angle follows the order :

$$NH_4^+ > NH_3 > NH_2^-$$

6. The dipole moment of cis $C_2H_2Cl_2$ isomer is more than that of trans isomer.
7. N_2^+ has greater bond dissociation enthalpy than N_2 molecule.
8. Out of MgO and CaO, MgO is harder.
9. The *d*-orbital involved in dsp^2 hybridisation is $d_{x^2-y^2}$.
10. The dipole moment of CH_3F is greater than that of CH_3Cl.

B. Complete the missing links

1. During the change : $O_2 \longrightarrow O_2^+ + e^-$, bond order changes from .... to ....
2. Ortho nitrophenol has .... hydrogen bond while *p*-nitrophenol has .... hydrogen bond.
3. In SF_4 molecule, S involves .... hybridisation.
4. The *d*-orbitals involved in sp^3d^2 hybridisation are .... and ....
5. The shape of ClF_3 molecule is ....
6. Out of H_2S, CO_2, BeF_2 and H_2O, the linear molecules are ....
7. The shape of BrF_5 molecule is ....
8. The number of lone pairs and bond pairs in XeF_4 molecule are .... and ....
9. The bond order in O_2^+ species is ....
10. Out of HF, HCl, HBr and HI, the lowest boiling point is of .... and highest boiling point is of ....

C. Choose the correct alternative

1. The bond in peroxide ion is *weaker / stronger* than in superoxide ion.
2. In N_2 molecule, energy of $\pi2p_x$ and $\pi2p_y$ MOs are *lower / higher* than $\sigma2p_z$ MO.
3. The bond length of CO^+ is *more / less* than CO.
4. N_2 molecule is *paramagnetic / diamagnetic.*
5. The *d*-orbital involved in sp^3d hybridisation is $d_{z^2} / d_{x^2-y^2}$.
6. Bond angle of H_2O is *more / less* than that of H_2S.
7. The dipole moment of ortho dichlorobenzene is *more / less* than meta dichlorobenzene.
8. The bond length of sp^3(C—H) is *more / less* than sp^2(C—H) bond.
9. The shape of XeF_4 molecule is *tetrahedral / square planar*.
10. Dipole moment of NF_3 molecule is *more / less* than NH_3 molecule.
11. $[NiCl_4]^{2-}$ ion has *square planar / tetrahedral* geometry.
12. The bond angle of NO_2^+ is *more / less* than NO_2^-.
13. O_3 and NO_2^- are *isoelectronic / not isoelectronic.*
14. Bond order of O_2^+ is *1.5 / 2.5.*
15. Ice has *less / more* density than water.

Answers QUICK MEMORY TEST

A. Say True or False

1. True
2. **False :** Shape of IF_7 is pentagonal bipyramidal.
3. **False :** Bond order of CO molecule is 3.
4. **False :** NF_3 has lower dipole moment than NH_3.
5. True
6. True
7. **True :** N_2 has bond order 3 and N_2^+ has bond order of 2.5.
8. **True :** Mg^{2+} ions are smaller than Ca^{2+} ions and therefore, lattice energy of MgO is larger and it is harder.
9. True
10. **False :** Though C—F bond is more polar than C—Cl bond due to greater electronegativity of F than Cl but C—F bond length is much smaller than C—Cl bond length.

B. Complete the missing links

1. 2, 2.5 **2.** intramolecular, intermolecular
3. sp^3d **4.** $d_{x^2-y^2}$, d_{z^2}
5. T-shaped **6.** BeF_2, CO_2
7. Square pyramidal **8.** 2, 4
9. 2.5 **10.** HCl, HF.

C. Choose the correct alternative

1. weaker **2.** lower **3.** less
4. diamagnetic **5.** d_{z^2} **6.** more
7. more **8.** more **9.** square planar
10. less **11.** square planar **12.** more
13. isoelectronic **14.** 2.5 **15.** less.

HOTS Higher Order Thinking Skills & Advanced Level

QUESTIONS WITH ANSWERS

Q.1. Which is expected to have the highest melting point :

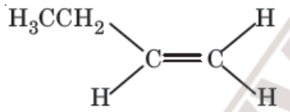
NH_3, $(CH_3)_3N$ or PH_3 ? Explain why ?

Ans. NH_3 has the strongest intermolecular forces (hydrogen bonding) and therefore, is expected to have the highest melting point.

Q.2. Which of the following has higher dipole moment and why ?

But-1-ene or But-1-yne

Solution: The structure of 1-butene and 1-butyne are:



But-1-ene

$H_3C—CH_2—C \equiv CH$

But-1-yne

In but-1-ene, each doubly bonded C-atom is sp^2 hybridised while in but-1-yne, each triply bonded C-atom is *sp* hybridised. Since *sp*-C is more electronegative than a sp^2C atom, therefore 1-butyne has higher dipole moment.

Q.3. Explain why melting point of NaCl is higher than that of $AlCl_3$.

Ans. Melting point of NaCl is higher than that of $AlCl_3$ because of strong electrostatic forces between oppositely charged ions. On the other hand, $AlCl_3$ is a covalent compound with lesser forces of attraction.

Q. 4. Silver halides have low solubilities in water as compared to alkali metal halides. Explain.

Ans. Silver halides are least soluble in water though their lattice energies are almost of the same order as that of highly soluble alkali metal halides. This can be explained on the basis of the outer electronic configuration of silver ion. The electronic configuration of Ag^+ is : $4d^{10}\,5s^0\,5p^0$. The electronic configuration of alkali metal ions, Li^+, Na^+ or K^+ is ns^0. We know that the *d*-electrons screen the nuclear charge from the outer electrons less effectively than *s* and *p*-electrons because of their poor penetration. Therefore, the effective nuclear charge, experienced by Ag^+ ion is much more than effective nuclear charge in alkali metal ions. Due to greater nuclear charge, the Ag^+ ion polarises the halide ion more strongly than alkali metal ion. Hence, it undergoes appreciable change from pure ionic character to covalent character. Because of the covalent character, the silver halides are less ionic and consequently their solubility in polar water is low.

Q.5. Which homonuclear diatomic molecule besides O_2 is paramagnetic ?

Ans. B_2 because its electronic configuration is:

$$B_2 : KK(\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p_x)^1(\pi 2p_y)^1$$

Q.6. Distinguish between antibonding and nonbonding orbitals.

Ans. Antibonding orbitals have higher energies than the highest atomic orbital from which they are formed. On the other hand, nonbonding orbitals have the same energy as the atomic orbitals from which they are formed.

Q.7. Anhydrous $AlCl_3$ is covalent but $AlCl_3 . 6H_2O$ is ionic in nature. How would you account for this?

Ans. Anhydrous $AlCl_3$ is covalent while $AlCl_3 . 6H_2O$ is ionic in nature. The third ionisation energy of aluminium is very high. Therefore, a large amount of energy is needed to convert Al atom into Al^{3+} ion.

$$Al(g) + 5114 \text{ kJ mol}^{-1} \longrightarrow Al^{3+}(g) + 3e^-$$

Therefore, aluminium prefers to form covalent bonds with chlorine atoms forming covalent $AlCl_3$. However, when dissolved in water, it undergoes hydration liberating hydration energy.

$$AlCl_3 + 6H_2O \longrightarrow \underset{\text{Hydrated}}{AlCl_3 . 6H_2O} + \text{Energy}$$

$$[Al(H_2O)_6]^{3+} + 3Cl^-$$

The hydration energy released provides energy for the removal of 3 electrons from aluminium atom. In fact, aluminium does not exist as simple aluminium ion (Al^{3+}) but in the form of a complex ion $[Al(H_2O)_6]^{3+}$. Thus, hydrated aluminium chloride is ionic in nature.

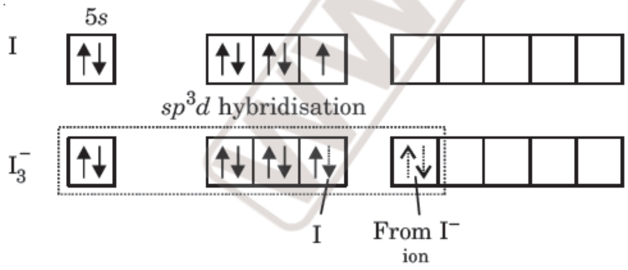
Q.8. Cu^+ and Na^+ are of same size but CuCl is insoluble while NaCl is soluble in water. Explain.

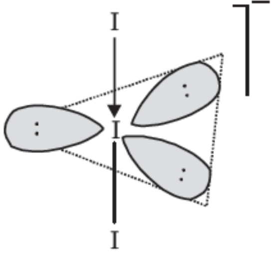
Ans. In NaCl, the hydration energy is sufficient to overcome the lattice energy of ionic NaCl. Hence NaCl is soluble in water. The high hydration energy of NaCl is because of relatively high ionic character of NaCl with the result that water dipoles interact strongly with Na^+ and Cl^- ions.

On the other hand, CuCl has sufficiently covalent character because of greater polarization of Cu^+ ion *(refer Q.4)* . As a result of covalent character, its hydration energy is low and is not sufficient to overcome the lattice energy of CuCl. Consequently, it is insoluble in water.

Q.9. Account for the linear shape of I_3^- ion.

Ans. The central I atom has the ground state electronic configuration as $5s^2\ 5p^5$. It involves sp^3d hybridization involving one 5*s*, three 5*p* and one vacant 5*d* orbital. The half filled sp^3d hybrid orbital forms a covalent bond with one I atom and an empty sp^3d hybrid orbital accepts an electron pair from I^- ion to form a coordinate bond. Thus, the geometry of the molecule is trigonal bipyramidal in which three positions are occupied by lone pairs.

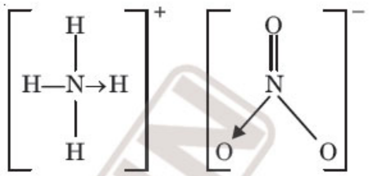




Because of the equivalent positions of lone pairs the resulting I_3^- ion is linear.

Q.10. Indicate the types of bonds present in NH_4NO_3 and state the mode of hybridisation of two N atoms.

Ans.



NH_4^+ ion contains three covalent bonds and one dative bond (formed by the donation of lone pair of electrons on N in NH_3 to H^+ ion).

NO_3^- ion contains covalent and dative bonds.

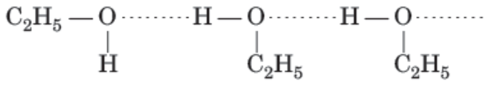
The bond between NH_4^+ and NO_3^- is ionic.

N of NH_4^+ ion is sp^3 hybridised and the shape of NH_4^+ ion is tetrahedral. N of NO_3^- ion is sp^2 hybridised and the shape of NO_3^- ion is planar.

Q.11. Which one has high boiling point and why ?

Ethyl alcohol or dimethyl ether.

Ans. Ethyl alcohol (C_2H_5OH) has higher boiling point because of hydrogen bonding in its molecules.

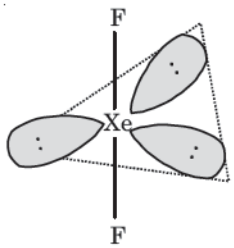


$$C_2H_5-\underset{|}{\underset{H}{O}}\cdots\cdots H-\underset{|}{\underset{C_2H_5}{O}}\cdots\cdots H-\underset{|}{\underset{C_2H_5}{O}}\cdots\cdots$$

There is no hydrogen bonding in dimethyl ether ($C_2H_5OC_2H_5$).

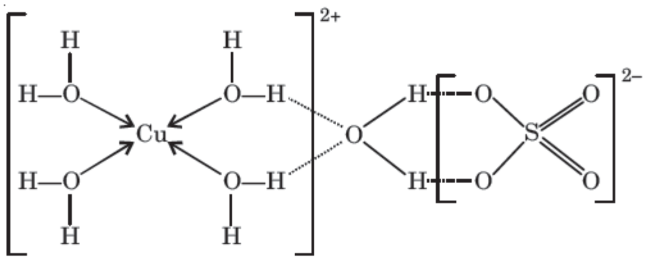
Q.12. XeF_2 molecule is linear molecule but it is sp^3d hybridized. Why ?

Ans. Due to sp^3d hybridisation, it has trigonal bipyramidal geometry in which three positions are occupied by lone pairs of electrons. The lone pairs are present in equatorial positions and their resultant effect is zero. As a result, the bonds are formed by axial Xe—F bonds only which are at an angle of 180° to each other.



Q.13. Name and represent the types of bonds present in $CuSO_4 . 5H_2O$.

Ans. $CuSO_4 . 5H_2O$ has ionic, covalent, coordinate and hydrogen bonds as shown ahead :

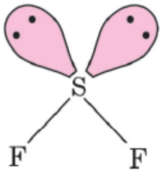


In $CuSO_4 . 5H_2O$, four H_2O molecules are bonded to Cu^{2+} ion by coordinate bonds whereas fifth H_2O molecule is linked by hydrogen bonds between two coordinated H_2O molecules and two oxygen atoms of sulphate ion.

Q.14. BeF_2 molecule is linear while SF_2 is angular though both are triatomic.

Ans. In BeF_2, Be is surrounded only by 2 electron bond pairs and therefore, the molecule is linear. On the other hand, in SF_2, the central atom S, is surrounded by 2 bond pairs and 2 lone pairs. Since it is surrounded by 4 electron pairs, the geometry is expected to be tetrahedral with two positions occupied by lone pairs.

F—Be—F



2 bond pairs (Linear)

2 bond pairs, 2 lone pairs (Angular)

Because of the larger repulsions of lone pair-bond pair, the bond angle is less than 109.5° and the resultant molecule is angular.

Q.15. Is the bond order in superoxide ion more or less than in peroxide ion. Explain on the basis of MO theory.

Ans. The MO configuration of superoxide ion (O_2^-) is :

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

$$\text{Bond order} = \frac{8-5}{2} = 1\frac{1}{2}$$

The MO configuration of peroxide ion is (O_2^{2-}) is

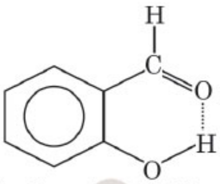
$$KK(\sigma 2s)^2(\sigma^*2s)^2(\sigma 2p_z)^2(\pi 2p_x)^2(\pi 2p_y)^2(\pi^*2p_x)^2(\pi^*2p_y)^2$$

$$\text{Bond order} = \frac{8-6}{2} = 1$$

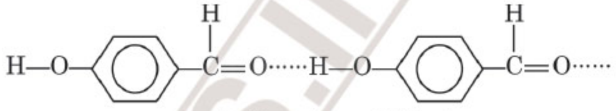
So, bond order in superoxide ion is more than in peroxide ion.

Q.16. Explain why o-hydroxybenzaldehyde is a liquid at room temperature while *p*-hydroxy-benzaldehyde is a high melting solid.

Ans. In o-hydroxybenzaldehyde, there is intramolecular hydrogen bonding which further prevents association of the molecules. However, in *p*-hydroxy benzaldehyde, there is intermolecular hydrogen bonding and therefore, there is association among the molecules :



o-hydroxybenzaldehyde
(intramolecular hydrogen bonding)



p-hydroxybenzaldehyde
(intermolecular hydrogen bonding)

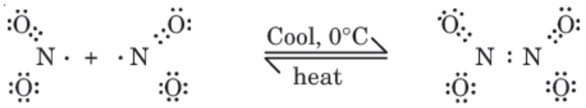
Thus, because of larger association, *p*-hydroxy benzaldehyde is a solid at room temperature but *o*-hydroxybenzaldehyde is a liquid because of less association.

Q.17. Nitrogen dioxide (NO_2) is paramagnetic at room temperature. When a sample of the gas is cooled below 0°C, its molecular weight increases and it loses its paramgnetism. When it is reheated, the behaviour is reversed.

(*i*) Using electron dot structure, write an equation which accounts for these observations.

(*ii*) How does this phenomenon differ from resonance?

Ans. (*i*) NO_2 has one unpaired electron and is therefore, paramagnetic in nature. On cooling it forms dimer N_2O_4 which has higher molecular mass and is diamagnetic. This is represented as :

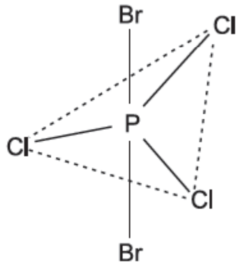


(*ii*) This is an equilibrium reaction and differs from resonance.

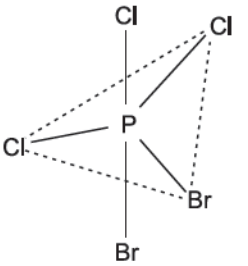
Q.18. Draw three possible geometrical structures of PBr_2Cl_3 and predict which of these have dipole moments.

Ans.

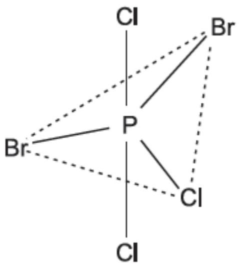
(*i*)



(*ii*)



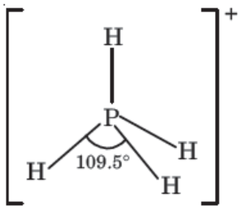
(*iii*)

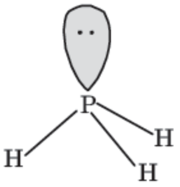


Structures (*ii*) and (*iii*) have dipole moments.

Q.19. Bond angle in PH_4^+ is higher than that in PH_3 why ?

Ans. Both PH_4^+ and PH_3 involve sp^3 hybridisation of P atom. In PH_4^+ all the four orbitals are bonded, whereas in PH_3 there is a lone pair of electrons on P. In PH_4^+, the HPH bond angle is tetrahedral angle of 109.5°. But in PH_3, lone pair-bond pair repulsion is more than bond pair-bond pair repulsion so that bond angles become less than normal tetrahedral angle 109.5°. The bond angle in PH_3 has been found to be about 93.6°.





Q.20. Why does PCl_5 exist as $[PCl_4]^+[PCl_6]^-$ in the crystalline state ?

Ans. PCl_5 has unsymmetrical structure because of different axial and equatorial bonds. Therefore, it is unstable and it changes to tetrahedral $[PCl_4]^+$ and octahedral $[PCl_6]^-$ ions, which have stable geometries.

Q.21. Explain the observations that the bond length in N_2^+ is 0.02Å larger than in N_2 while the bond length in NO^+ is 0.09Å less than in NO.

Ans. The electronic configurations are :

$$N_2 : KK(\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x)^2 (\pi 2p_y)^2 (\sigma 2p_z)^2;\ \text{B.O.}\ \frac{8-2}{2} = 3$$

$$N_2^+ : KK(\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x)^2 (\pi 2p_y)^2 (\sigma 2p_z)^1;\ \text{B.O.}\ \frac{7-2}{2} = 2.5$$

$$NO : KK(\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x)^2 (\pi 2p_y)^2 (\sigma 2p_z)^2 (\pi^* 2p_x)^1;\ \text{B.O.}\ \frac{8-3}{2} = 2.5$$

$$NO^+ : KK(\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x)^2 (\pi 2p_y)^2 (\sigma 2p_z)^2;\ \text{B.O.}\ \frac{8-2}{2} = 3$$

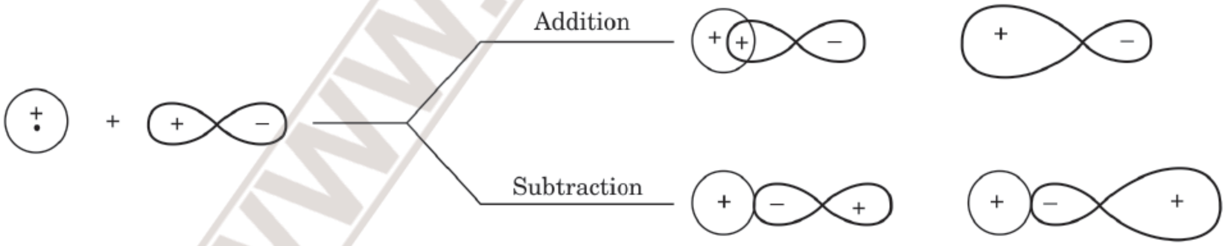
N_2 molecule has stronger bond than N_2^+ and therefore, N_2^+ has larger bond length than N_2. NO has weaker bond than NO^+ and therefore, NO^+ has smaller bond length than NO. Moreover, in comparison to ionization of N_2 which involves the loss of electron from bonding MO, the ionization of NO involves loss of electron from antibonding MO. Therefore, the decrease in bond length from NO to NO^+ is more than increase in bond length from N_2 to N_2^+.

Q.22. Which of the following combinations of orbitals are allowed in LCAO method (considering z-axis to be molecular axis) and sketch the shapes of MOs formed by their addition and subtraction :

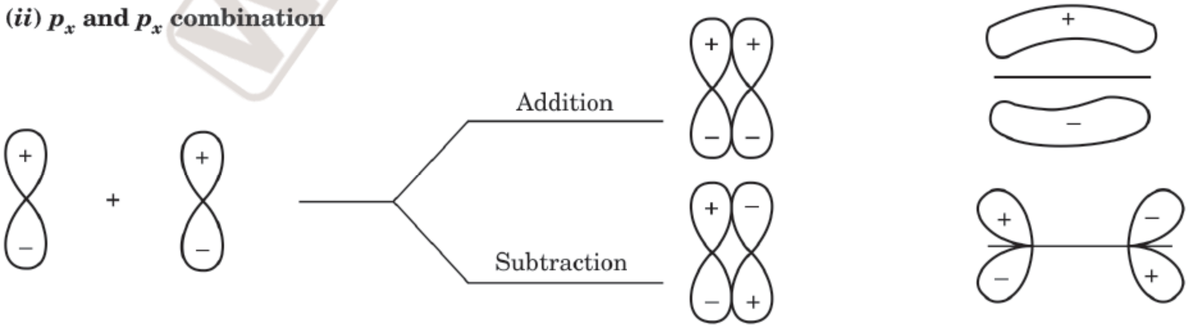
(*i*) *s* and p_z (*ii*) p_x and p_x (*iii*) p_z and p_y (*iv*) *s* and p_x

Ans. The allowed combinations are (*i*) *s* and p_z and (*ii*) p_x and p_x. Other combinations (*iii*) and (*iv*) are not allowed because they have zero overlap.

(*i*) *s* and p_z combination



(*ii*) p_x and p_x combination



Revision Exercises

Very Short Answer Questions *carrying 1 mark*

1. Why are the noble gases monoatomic ?

2. Can a non-polar molecule have polar bonds ? Explain with an example.

3. Give one example each for a compound with (*a*) an ionic bond (*b*) a covalent bond.

4. Write Lewis dot structure for HCOOH.

5. Which hybrid orbitals are used by carbon atoms in $H_3C—CH = CH_2$

6. Write formal charges of the atoms in nitrite ion.

7. Which out of the two molecules OCS and CS_2 has a higher dipole moment and why ?

8. An element A has the electronic configuration $1s^22s^22p^63s^2$ and another element B has the electronic configuration $1s^22s^22p^63s^23p^5$. What type of bond is formed between A and B ? Give its Lewis structure.

9. Define resonance.

10. How does the hybridisation of carbon atom in $CH_2 = CH_2$ change when it is hydrogenated to CH_3CH_3 ?

11. Give two examples of molecules containing coordinate bond.

12. What are the shapes of (*i*) BF_3 and (*ii*) NH_3 molecules ?

13. Which of the two bonds : ionic or covalent is directional ?

14. Can a π-bond be formed without the formation of a σ-bond. How many σ-and π-bonds are formed in acetylene?

15. Draw Lewis structure of O^{2-} and N^{3-} ions.

16. Give bond angles in H_2O, CH_4 and SF_6 molecules.

17. Name the factors which favour the formation of an ionic bond.

18. Define dipole moment. What are its units ?

19. How many σ-and π-bonds are present in naphthalene ?

20. Out of MgO and NaCl, which has higher lattice energy ?

21. What is meant by bond pair of electrons and lone pair of electrons ?

22. Define electronegativity and dipole moment.

23. Give one example each of a tetraatomic molecule which is

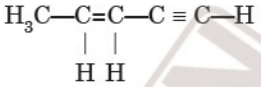
(*i*) Polar (*ii*) Non-polar.

24. Give one example each of a molecule having

(*i*) 6 bond pairs

(*ii*) 7 bond pairs around the central atom.

25. What is the total number of sigma bonds and pi bonds in



$$H_3C—\underset{H}{\underset{|}{C}}=\underset{H}{\underset{|}{C}}—C\equiv C—H$$

26. What shapes are associated with sp^3d and sp^3d^2 hybrid orbitals ?

27. How is paramagnetic character of a compound related to the number of unpaired electrons ?

28. Which out of H_2^- and H_2^+ is more stable and why ?

29. Which *d*– orbitals are involved in sp^3d^2 hybridisation in SF_6 ?

30. Write the molecular orbital configuration of a molecule having bond order of three.

31. Which out of O_2^+ and O_2^- is more stable ?

32. Arrange the following molecular species in order of increasing stability :

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

33. What is the shape of SF_6 molecule ?

34. Give one example of a molecule involving sp^3d hybrdisation.

35. Although chlorine has the same electronegativity as nitrogen, it does not form hydrogen bonding. Explain.

36. Why does formic acid exist as dimer ?

37. Why does KHF_2 exist but KCl_2 does not ?

38. State the type of hybrid orbitals associated with (*i*) P in PCl_5 and (*ii*) S in SF_6. *(D.S.B. 2001)*

39. Which one of two : O_2^- and O_2^{2-} has higher bond order and why ?

40. What is the effect of the following ionization processes on the bond order in C_2 and O_2 ?

(*i*) $C_2 \longrightarrow C_2^+ + e^-$ (*ii*) $O_2 \longrightarrow O_2^+ + e^-$ *(A.I.S.B. 2002)*

41. What is the effect on the interatomic bond length of the following ionization processes ?

(*i*) $N_2 \longrightarrow N_2^+ + e^-$ (*ii*) $C_2 \longrightarrow C_2^+ + e^-$ *(A.I.S.B. 2002)*

42. Which one of the following has highest bond order ?

N_2, N_2^+ or N_2^- *(A.I.S.B. 2002)*

43. Draw a diagram showing the formation of bonding and anti-bonding molecular orbitals by LCAO in homonuclear hydrogen molecule. *(D.S.B. 2004)*

44. Which of the two : ice or water has lower density ?

45. Do N_2^+ and O_2^+ have same bond order ?

46. Define bond length.

Short Answer Questions *carrying 2 or 3 marks*

1. Explain the formation of a chemical bond.

2. Explain the formation of a covalent bond. State two factors which influence the formation of a covalent bond.

3. Write the favourable factors for the formation of ionic bond ?

4. Define octet rule. Write its significance and limitations.

5. What do you understand by a chemical bond ? Why do atoms combine to form compounds ?

6. Draw Lewis symbols for the following elements :

B, Ge, Si, Ar, Ca, K, As, Br.

7. Give one example of a compound containing double bond and one containing a triple bond.

8. Explain that whereas H_2 and F_2 are non-polar, HF is polar.

9. Draw the orbital representation of the molecules:

HF, H_2O and NH_3.

10. Write the Lewis dot structures of (*i*) CCl_4 (*ii*) PH_3 and (*iii*) BCl_3. Is the octet rule is obeyed in these structures ?

11. Draw the shapes of the following hybrid orbitals :

sp, sp^2, sp^3

12. Considering Z-axis as the internuclear axis, which out of the following will form a sigma bond :

(*i*) $1s$ and $1s$ (*ii*) $1s$ and $2p_z$ (*iii*) $2p_x$ and $2p_x$

(*iv*) $2p_x$ and $2p_y$ (*v*) $2p_y$ and $2p_y$

13. Give the Lewis dot structures of NH_3, CH_4 and SO_3.

14. Draw electron dot structures of the following :

(*i*) OF_2 (*ii*) C_2H_2

(*iii*) PCl_3 (*iv*) H_2O_2.

15. What is octet rule ? List important exceptions to octet rule.

16. Give the number and types of various bonds in acetylene molecule. Name the type of overlap responsible for each bond.

17. Draw dipole moment diagrams showing polarity of individual bonds and resultant dipole of the following :

(*i*) H_2O (*ii*) CO_2

(*iii*) BeF_2 (*iv*) BF_3.

18. Describe a co-ordinate bond, giving one example. How does it differ from a covalent bond ?

19. Give a schematic representation of various attractive and repulsive forces when two hydrogen atoms approach each other to form a molecule of hydrogen.

20. The dipole moment of hydrogen halides decreases from HF to HI. Explain this trend.

21. Write the formal charges of the atoms in

(*i*) hydroxide ion (*ii*) carbonate ion

(*iii*) nitrite ion.

22. Sketch the bond moments and resultant dipole moments in the following molecules :

PCl_3, H_2O, NH_3, NF_3

23. Write resonance structures for SO_3, NO_2 and NO_3^-.

24. What is polar covalent bond ? Give two examples of compounds containing polar covalent bonds.

25. What is resonance ? What are the guidelines for writing resonating structures. Out of the following four resonance structures for the CO_2 molecule, which are important for describing the bonding in the molecules and why ?

$O{=}C{=}O$ 1 $\quad$ $\overset{+}{O}{\equiv}C{-}\overset{-}{O}$ 2

$\overset{-}{O}{\equiv}C{-}\overset{+}{O}$ 3 $\quad$ $O{-}C{-}\overset{-}{O}$ 4

26. Which of the two : KCl or Cl_2 has higher boiling point and why ?

27. Presence of lone pairs distorts the geometry of a molecule. Explain with example.

28. What do you understand by the term hybridisation ? Using the concept, explain the shapes of C_2H_4 and C_2H_2.

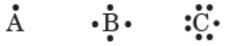
29. Define hybridisation. Discuss the bonding in acetylene molecule on the basis of hybridisation.

30. Write resonance structures for SO_3, NO_2 and NO_3^-.

31. Write the significance and applications of dipole moment.

32. Name the two bonds present in oxygen molecule and compare their strengths.

33. Three elements have the following Lewis symbols :



(*a*) Place the elements in the appropriate group of the periodic table.

(*b*) Which elements are most likely to form ions ? What is the expected charge on the ions ?

(*c*) Write the formulae and Lewis structures of the covalent compounds formed between:

(*i*) A and B (*ii*) A and C.

34. Explain the difference between sigma bond and pi-bond.

35. Define lattice enthalpy. How is it related to the stability of an ionic compound ?

36. What are the guidelines of writing resonating structures?

37. Explain sp^2 hybridisation and discuss the geometry of a molecule involving this type of hybridisation.

38. How do you account for equal bond lengths in ozone molecule ?

39. Define dipole moment. How does this help to predict the geometries of H_2O and CO_2 ?

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

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

42. Explain with the help of suitable example, polar covalent bond.

43. In each of the following pairs, predict which has higher value of the property mentioned :

(*i*) HF, HCl : Polar character
(*ii*) NH_3, H_2O : Bond angle
(*iii*) KCl, KF : Lattice enthalpy
(*iv*) NF_3, NH_3 : Dipole moment
(*v*) C_2H_2, C_2H_4 : *s*-character in the hybridisation of carbon

44. Explain the term dipole moment. Name two molecules which have dipole moment and two molecules which do not have dipole moment. What is the significance of dipole moment ?

45. Using the concept of hybridisation, explain the shapes of BF_3, C_2H_4 and C_2H_2 molecules.

46. The electronic configurations of five neutral atoms are given below :

A : $1s^2\ 2s^2\ 2p^6\ 3s^2$;
B : $1s^2\ 2s^2\ 2p^6\ 3s^1$
C : $1s^2\ 2s^2\ 2p^1$;
D : $1s^2\ 2s^2\ 2p^3$
E : $1s^2\ 2s^2\ 2p^6$

Write the empirical formula for the substances containing:

(*i*) A and D (*ii*) B and D
(*iii*) D and D (*iv*) E and E.

47. Each carbon-oxygen bond in CO_2 molecule is polar and the molecule is non-polar. Explain.

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

49. Draw electron dot representation of :

(*i*) acetylene
(*ii*) ammonia.

50. What is dipole moment ? How does it affect the polarity of the molecule ? Which of the following molecules do you expect to be polar ?

CO, CCl_4, H_2O, BF_3, NH_3 and CO_2.

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

52. Each carbon-oxygen bond in carbon dioxide molecule is polar but the molecule itself is non-polar. Explain.

53. CO_2 and H_2O both are triatomic molecules but there is large difference in their dipole moment values. Explain.

54. Explain the following :

(*a*) HCl is a covalent compound but it ionises in the solution.

(*b*) The molecule of $MgCl_2$ is linear whereas that of $SnCl_2$ is angular.

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

56. Why is it that in SF_4 molecule, the lone pair of electrons occupies an equatorial position in the overall trigonal bipyramidal arrangement in preference to an axial position ?

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

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

59. Explain how does the valence bond theory account for

(*i*) a carbon–carbon double bond (C=C)

(*ii*) a carbon–carbon triple bond (C≡C)

60. What do you understand by a molecular orbital ? What is the maximum number of electrons that can occupy a molecular orbital?

61. What do you understand by bonding and antibonding molecular orbitals ? Calculate the bond order for O_2^+ and O_2.

62. Discuss the conditions necessary for the combination of atomic orbitals. Sketch and discuss the combination of *p*-atomic orbitals to form molecular orbitals.

63. Draw molecular orbital energy level diagram for nitrogen molecule.

64. Using MO diagram and occupancy of electrons in orbitals, arrange the following molecular species in increasing order of their stabilities :

(*i*) H_2 (*ii*) H_2^- (*iii*) H_2^+

65. Fill in the blanks :

(*i*) During the process : $O_2 + e^- \longrightarrow O_2^-$, the electron is added to the .... MO.

(*ii*) The bond order in O_2^+ is .... than in O_2.

(*iii*) In O_2 molecule there are .... electrons in antibonding valence MOs.

66. Draw energy level diagrams to show that N_2 has triple bond, O_2 has double bond, F_2 has single bond and Ne_2 has no bond.

67. Is it correct to say that bond order always increases when an electron is lost ?

68. Compare the relative stability of the following species and indicate their magnetic properties (diamagnetic or paramagnetic)

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

69. Arrange the following species in order of increasing stability :

Li_2, Li_2^+ and Li_2^-

Justify your choice with a molecular orbital diagram.

70. How does molecular orbital theory account for the following ?

(*a*) Bond order of N_2 is greater than N_2^+ but the bond order of O_2 is less than that of O_2^+.

(*b*) Be_2 does not exist.

71. Sketch the shapes of MOs obtained by the overlap of

(*i*) two *s*-orbitals

(*ii*) end on overlap of two *p*-orbitals

(*iii*) sidewise overlap of two *p*-orbitals.

72. What is hybridisation ? What type of hybridisations are possible in the following geometries ?

(*i*) Square planar

(*ii*) Trigonal bipyramidal

(*iii*) Octahedral.

73. On the basis of hybridisation, discuss the structures of

(*i*) PCl_5

(*ii*) IF_7

(*iii*) SF_6.

74. Calculate the bond order of O_2^- and O_2^{2-} and explain their magnetic character.

75. Explain the following :

(*i*) O_2^- is paramagnetic but O_2^{2-} is not.

(*ii*) N_2 has higher bond order than NO.

76. Compare the relative stability of the following species and comment on their magnetic (diamagnetic or paramagnetic) behaviour :

O_2^- and N_2^+

Long Answer Questions *carrying 5 marks*

1. Explain the formation of hydrogen molecule on the basis of electrostatic interactions giving potential energy diagram. Explain why He_2 is not possible.

2. Discuss the formation of covalent bond according to orbital concept. Draw orbital overlap diagram for each of the following molecules :

(*a*) HF (*b*) NH_3 (*c*) C_2H_4

(*d*) BF_3 (*e*) OF_2.

3. Identify the type of bonds you would expect in :

(*a*) water (*b*) silicon

(*c*) aluminium (*d*) diamond

(*e*) chlorine.

4. What do you understand by electronegativity ? How is it useful in predicting polarity of molecules ?

5. Discuss the shapes of the following molecules on the basis of VSEPR theory :

(*i*) CH_4

(*ii*) PF_5

(*iii*) NH_3

(*iv*) H_2O

(*v*) SF_6.

6. Write short notes on

(*i*) Resonance

(*ii*) Coordinate covalent bond

(*iii*) σ and π bonds.

7. What is lattice energy ? Discuss Born Haber cycle for the determination of lattice energy of sodium chloride crystal.

8. Discuss the shape of the following molecules on the basis of VSEPR model

(*i*) $BeCl_2$

(*ii*) BCl_3

(*iii*) $SiCl_4$

(*iv*) AsF_5

(*v*) H_2S

(*vi*) PH_3

9. What is dipole moment ? Discuss its important applications.

10. What is hybridisation ? Discuss different types of hybridisation undergone by carbon.

11. With the help of molecular orbital theory, show that N_2 molecule has triple bond, O_2 molecule has double bond while F_2 molecule has single bond. Compare their bond strengths.

12. (*a*) Distinguish between the following :

(*i*) Bonding and antibonding MOs.

(*ii*) Sigma and pi bonds.

(*b*) What is hybridisation ? Discuss the shapes of the following on the basis of concept of hybridisation:

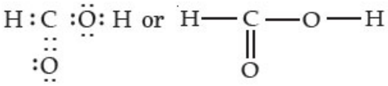
(*i*) SF_6 (*ii*) PF_5 (*iii*) $[Ni(CN)_4]^{2-}$

Hints & Answers for Revision Exercises

Very Short Answer Questions

2. Yes. Though the bonds in a molecule are polar, yet the arrangement of bonds is such that the overall polarity is zero. For example, CO_2 molecule has net zero dipole moment, but each CO bond is polar.

3. (*a*) Sodium chloride (*b*) Methane (CH_4)

4.


5. sp^3, sp^2, sp^2

7. OCS has higher dipole moment

8. Ionic bond. $A^{2+}\,[\,B\,]^-_2$

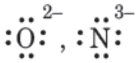
10. From sp^2 ($CH_2 = CH_2$) to sp^3 ($CH_3 — CH_3$)

11. H_3O^+, O_3

12. (*i*) Trigonal planar (*ii*) Pyramidal

13. Covalent bond

14. No, σ-bonds = 3, π-bonds = 2

15.


16. $H_2O = 104.5°$, $CH_4 = 109.5°$, $SF_6 = 90°$.

19. $\sigma = 19, \pi = 5$

20. MgO

23. (*i*) NH_3 (*ii*) BF_3

24. (*i*) SF_6 (*ii*) IF_7

25. $\sigma = 10, \pi = 3$

26. Trigonal bipyramidal, octahedral.

27. Larger the number of unpaired electrons, greater will be paramagnetic character

28. H_2^+ because it contains electrons only in bonding MOs.

29. $d_{x^2-y^2}$ and d_{z^2}

30. For N_2 : $KK\,(\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p_x)^2(\pi 2p_y)^2(\sigma 2p_z)^2$

31. O_2^+ because it has higher bond order (2.5) than O_2^- (1.5).

32. $N_2^{2-} < N_2^- < N_2^+ < N_2$

33. Octahedral

34. PF_5

35. The size of Cl is larger than N and therefore, it cannot form effective hydrogen bonding.

36. Due to hydrogen bonding.

37. Due to hydrogen bonding in HF as :

H—F.....H—F.....H—F.....

it can exist as HF_2^- ion and therefore forms KHF_2.

But there is no hydrogen bonding in HCl and it cannot form HCl_2^- ion.

39. (*i*) sp^3d (*ii*) sp^3d^2

40. (*i*) decreases (*ii*) increases

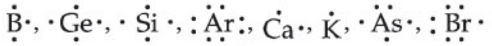
41. (*i*) increases (*ii*) decreases

42. N_2

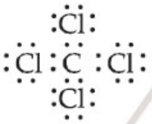
44. ice.

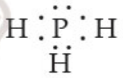
45. Yes, bond order in both N_2^+ and O_2^+ is 2.5.

Short Answer Questions *Carrying 2 or 3 marks*

6.


7. Double bond : O_2, Triple bond N_2.

10. (*i*)


(*ii*)


octet rule obeyed octet rule not obeyed

(*iii*)


octet rule obeyed

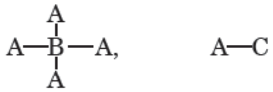
12. (*i*) and (*ii*)

25. 1 and 2 are important.

26. KCl because it is ionic compound having strong electrostatic forces of attraction.

33. (*a*) A (group 1), B (group 14), C (group 17)

(*b*) The elements likely to form ions are A and C, charges A^+, C^-

(*c*)


43. (*i*) HF (*ii*) NH_3

(*iii*) KF (*iv*) NH_3

(*v*) C_2H_2

46. (*i*) A_3D_2 (*ii*) B_3D

(*iii*) $D_2(D \equiv D)$ (*iv*) E(mono atomic)

48. NH_3

50. CO, H_2O, NH_3

51. Water — Covalent, Ammonia — Covalent, Ethylene — Covalent, Sodium chloride — Ionic

65. (*i*) $\pi^* 2p_x$ (*ii*) more (*iii*) four

67. Bond order may increase or decrease when an electron is lost depending upon whether the electron is lost from bonding or antibonding MO.

72. (*i*) dsp^2 (*ii*) dsp^3 (*iii*) sp^3d^2

75. (*i*) O_2^- : $KK(\sigma 2s)^2(\sigma^* 2s)^2(\sigma 2p_z)^2(\pi 2p_x)^2(\pi 2p_y)^2(\pi^* 2p_x)^2(\pi^* 2p_y)^1$

Paramagnetic due to the presence of 1 unpaired electron.

O_2^{2-} : $KK(\sigma 2s)^2(\sigma^* 2s)^2(\sigma 2p_z)^2(\pi 2p_x)^2(\pi 2p_y)^2(\pi^* 2p_x)^2(\pi^* 2p_y)^2$

It is diamagnetic.

(*ii*) N_2 : $KK\,(\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p_x)^2(\pi\, 2p_y)^2(\sigma\, 2p_z)^2$

$$\text{B.O.} = \frac{8-2}{2} = 3$$

NO : $KK\,(\sigma 2s)^2\,(\sigma^* 2s)^2(\pi 2p_x)^2(\pi 2p_y)^2(\sigma^* 2p_z)^2\,(\pi^* 2p_x)^1$

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

∴ N_2 has higher bond order than NO.

Competition File

Additional Useful Information and Objective Questions

ADDITIONAL USEFUL INFORMATION

☐ EFFECT OF ELECTRONEGATIVITY ON THE SHAPES OF MOLECULES

The electronegativities of the atoms present in the molecules have important effect on the shapes of the molecules.

(*i*) Effect of change of electronegativity of the central atom

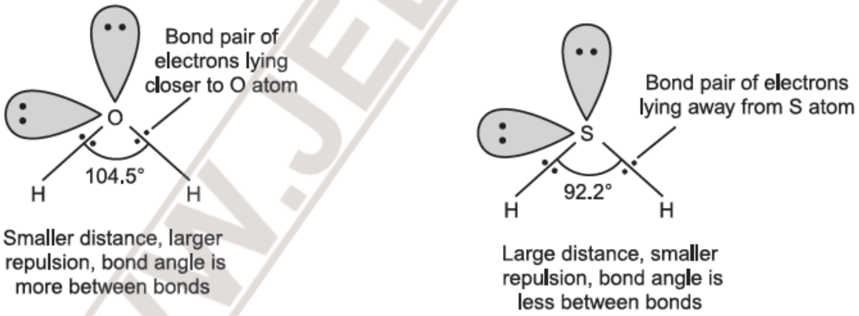
Consider the hydrides of Group VI elements. The hydrides H_2O, H_2S, H_2Se and H_2Te have four electron pairs (two bond pairs and two lone pairs) around the central atom. But their bond angles decrease in the order :

H_2O	H_2S	H_2Se	H_2Te
104.5°	92.6°	91°	90°

This may be easily explained in terms of electronegativities of the central atom as given below :

In the hydrides of Group VI elements, the central atom involves sp^3 hybridisation and is surrounded by four electron pairs; two lone pairs and two bond pairs. Due to the larger lone pair-lone pair repulsions, the bonded electron pairs are forced closer to each other and, therefore, the bond angle decreases from normal tetrahedral angle of 109.5°.

Now, as we move down the group from oxygen to tellurium, the size of the central atom goes on increasing and its electronegativity goes on decreasing. Consequently, the position of the bond pairs of electrons shifts more and more away from the central atom in moving from H_2O to H_2Te as shown in the figure. For example, as shown, the bond pair in O—H bond is closer to oxygen than the bond pair in S—H bond. As a result, the force of repulsion between the bonded pairs of electrons in H_2O is more than that in H_2S. In general, the force of repulsion between the bonded pairs of electrons decreases as we move from H_2O to H_2Te and, therefore, the bond angle also decreases in the same order.



Similar behaviour is observed in the case of hydrides of group V elements as given below :

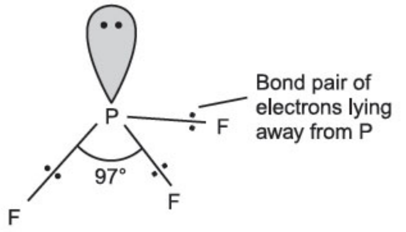
NH_3	PH_3	AsH_3	SbH_3
107°	104°	92°	92°

(*ii*) Effect of change of electronegativity of the bonded atom

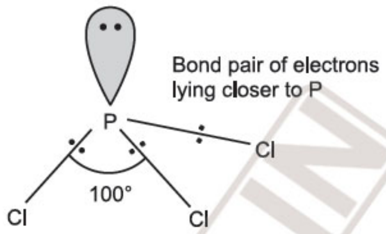
Take the example of halides of phosphorus (PX_3). The bond angles in these halides are observed as :

PF_3	PCl_3	PBr_3	PI_3
97°	100°	101.5°	100°

This can be explained on the basis of electronegativity of the atom attached to the central atom (*i.e.* halogen atom). In these molecules, P involves sp^3 hybridisation forming three sigma bonds and one position is occupied by a lone pair. The geometry may be described as pyramidal and as we move from PF_3 to PI_3, the electronegativity of the atom attached to the central phosphorus atom goes on decreasing. As a result, the bonding pair moves closer to the central atom as shown. For example, as shown in figure, the bond pair in PF_3 is away from P (closer to F) than the bond pair in PCl_3. Therefore, the repulsive effect between the bonding pairs increases and hence bond angle increases.



Large distance, smaller repulsion, bond angle is less between bonds



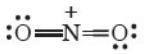
Smaller distance, larger repulsion, bond angle is greater between bonds

❑ EFFECT OF LONE PAIRS ON BOND ANGLE

The bond angle in NO_2, NO_2^+ and NO_2^- decreases as:

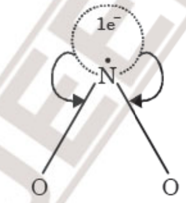
$$NO_2^+ > NO_2 > NO_2^-$$

The decreasing order of bond angle in NO_2^+, NO_2 and NO_2^- can be explained on the basis of presence of unshared electron and unshared electron pair. In NO_2^+, there is no unshared electron on N and therefore, the molecule is linear having bond angle of 180°. In NO_2, there is an unshared electron on N while in NO_2^-, there is an unshared electron pair on N-atom. The unshared electron pair causes more repulsion than an unshared electron. Therefore, the bond pairs in NO_2^- are forced more closer than in NO_2.

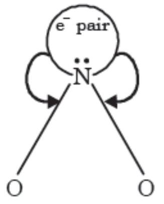


Linear

Bond angle = 180°



Bond angle = 132°



Bond angle = 115°

❑ CALCULATION OF TOTAL NUMBER OF BOND PAIRS AND LONE PAIRS AND PREDICTING SHAPES OF MOLECULES AND IONS

(*i*) Total no. of electron pairs around central atom

$= \frac{1}{2}$ (No. of valence electrons of the central atom + No. of atoms linked to central metal atom by single bonds).

For negative ions, **add** number of electrons equal to the units of negative charge on the ion to the number of valence electrons of the central atom and for positive ions **subtract** number of electrons equal to the units of positive charge from the valences electrons of the central atom.

(*ii*) No. of bond pairs (or shared pairs) = No. of atoms linked to central atom by single bonds.

(*iii*) No. of lone pairs = Total number of electron pairs – No. of bond pairs

Depending upon the number of electron pairs and the presence of lone pairs, shape can be predicted on the basis of Table 8 (Page 34).

Illustrations

ClF_3 : No. of valence electrons of the central Cl atom = 7
No. of electrons contributed by 3Cl atoms = 3

$\therefore$ Total no. of electron pairs around Cl atom = $\frac{7+3}{2} = 5$

No. of bond pairs = No. of atoms linked to Cl = 3

No. of lone pairs = 5 – 3 = 2

Thus, molecule has trigonal bipyramidal shape with two positions occupied by lone pairs. Hence, its shape is **T-shaped.**

For quick solution, we can use the abbreviations as:

No. of valence electrons around central atom = Valence electrons;

No. of electrons contributed by atoms linked by single bonds = single bonds;

Total number of electron pairs = *ep*, No. of bond pairs = *bp*, No. of lone pairs = *ep*.

SF_4 : Valence electrons = 6, No. of single bonds = 4

$$e.p = \frac{6+4}{2} = 5,\ bp = 4,\ lp\ 5-4 = 1$$

Since it has 5 *ep*, the shape will be pentagonal bipyramidal with one position occupied by lone pair. Hence, its shape is **see-saw.**

BrF_5 : Valence electrons = 7, single bonds = 5

$$e.p = \frac{7+5}{2} = 6,\ bp = 5,\ lp = 6-5 = 1$$

Since it has 6 *ep*, its geometry will be octahedral with one position occupied by a lone pair. Hence, it has **square pyramidal shape.**

NH_4^+ : Valence electrons = 5, single bonds = 4, unit positive charge = 1

$$e.p = \frac{5+4-1}{2} = 4,\ bp = 4,\ lp = 4-4 = 0$$

It has **tetrahedral shape.**

NH_2^- : Valence electrons = 5, single bonds = 2, unit negative charge = 1

$$e.p = \frac{5+2+1}{2} = 4,\ bp = 2,\ lp = 4-2 = 2$$

It has tetrahedral geometry with two positions occupied by lone pairs. Its shape is **bent** or **v-shape.**

XeF_4: Valence electrons = 8, single bonds = 4

$$e.p = \frac{8+4}{2} = 6,\ bp = 4,\ lp = 6-4 = 2$$

Since it has 6 *ep*, its geometry will be octahedral with two positions occupied by lone pairs. Hence, it has square **planar shape.**

PREDICTING TYPE OF HYBRIDISATION OF CENTRAL ATOM IN A MOLECULE / ION AND SHAPES OF MOLECULES

The structure of a molecule can be predicted on the basis of hybridisation. The type of hybridisation can be known by the following **general formula.**

$$N = \frac{1}{2}\left[\begin{array}{l}\text{No. of electrons in} \\ \text{valence shell of} \\ \text{of central atom}\end{array} + \begin{array}{l}\text{No. of monovalent} \\ \text{atoms}\end{array} - \begin{array}{l}\text{Charge on} \\ \text{cation}\end{array} + \begin{array}{l}\text{Charge} \\ \text{on anion}\end{array}\right]$$

or $N = \frac{1}{2}\ [V + M - C + A]$, where N is the number of orbitals hybridised.

For example,

Value of N :	2	3	4	5	6	7
Hybridisation :	sp	sp^2	sp^3	sp^3d	sp^3d^2	sp^3d^3

Competition File

In some cases, the hybrid orbitals may be occupied by lone pair of electrons. Number of lone pairs of electrons may be calculated as :

L = N – M – D, where, D is number of divalent atoms.

Illustrations :

⇒ **Type I :** Central atom is surrounded by monovalent atoms only *e.g.* BeF_2, BCl_3, CH_4, PCl_5, PCl_3, H_2O, NH_3, $TeCl_4$, SCl_2, ClF_3, SF_4, XeF_2, XeF_4, SF_6, etc.

e.g. **PF_5**

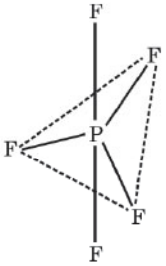
Here, V = 5, M = 5, C = 0, A = 0

$$N = \frac{1}{2}[5 + 5 - 0 + 0] = 5$$

***sp*³*d* hybridisation**

L = 5 – 5 = 0

No lone pair



Trigonal bipyramidal

ClF_3

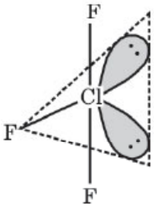
Here, V = 7, M = 3, C = 0, A = 0

$$N = \frac{1}{2}[7 + 3 - 0 - 0] = 5$$

***sp*³*d* hybridisation**

L = 5 – 3 – 0 = 2

It contains 2 lone pairs.



T-shaped

⇒ **Type II :** Central atom is surrounded by divalent atoms only *e.g.* SO_2, CO_2, CS_2, XeO_3, SO_3, etc.

e.g. **SO_3**

Here, V = 6, M = 0, C = 0, A = 0

$$N = \frac{1}{2}[6 + 0 - 0 + 0] = 3$$

***sp*² hybridisation**

L = 3 – 3 = 0

No lone pair.

Trigonal planar

XeO_3

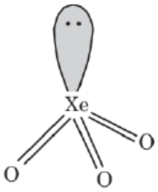
Here, V = 8, M = 2, C = 0, A = 0

$$N = \frac{1}{2}[8 + 0 + 0 - 0] = 4$$

***sp*³ hybridisation**

L = 4 – 3 = 1

It contains one lone pair.



Pyramidal

⇒ **Type III :** Central atom is surrounded by monovalent as well as divalent atoms *e.g.* $COCl_2$, $XeOF_2$, XeO_2F_2, $XeOF_4$, $POCl_3$ etc.

e.g. **$POCl_3$**

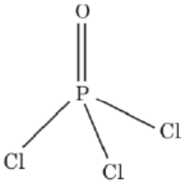
Here, V = 5, M = 3, C = 0, A = 0

$$N = \frac{1}{2}[5 + 3 - 0 + 0] = 4$$

***sp*³ hybridisation**

L = 4 – 3 – 1 = 0

No lone pair.



Tetrahedral

$XeOF_2$

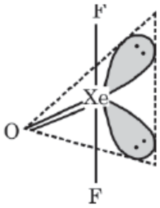
Here, V = 8, M = 2, C = 0, A = 0

$$N = \frac{1}{2}[8 + 2 - 0 + 0] = 5$$

***sp*³*d* hybridisation**

L = 5 – 2 – 1 = 2

Two lone pairs.



T-shaped

⇒ **Type IV :** Hybridisation in cations *e.g.* NH_4^+, CH_3^+, H_3O^+, etc.

e.g. **NH_4^+**

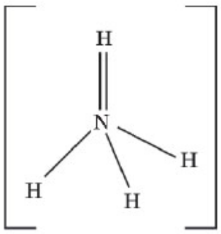
Here, $V = 5, M = 4, C = 1, A = 0$

$$N = \frac{1}{2}[5 + 4 - 1 + 0] = 4$$

***sp*³ hybridisation**

$L = 4 - 4 = 0$

No lone pair.



Tetrahedral

⇒ **Type V :** Hybridisation in anions *e.g.* CO_3^{2-}, NO_2^-, NO_3^-, SO_4^{2-}, PO_4^{3-}, ClO_3^-, ClO_4^-, etc.

e.g. **SO_4^{2-}**

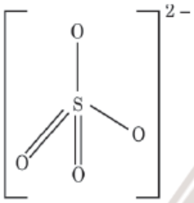
Here, $V = 6, M = 0, C = 0, A = 2$

$$N = \frac{1}{2}[6 + 0 - 0 + 2] = 4$$

***sp*³ hybridisation**

$L = 4 - 0 - 4 = 0$

No lone pair.



Tetrahedral

ClO_3^-

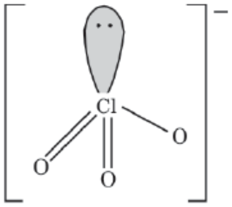
Here, $V = 7, M = 0, C = 0, A = 1$

$$N = \frac{1}{2}[7 + 0 - 0 + 1] = 4$$

***sp*³ hybridisation**

$L = 4 - 0 - 3 = 1$

One lone pair.



Pyramidal

⇒ **Type VI :** Hybridisation in complex ions e.g. I_3^-, ICl_2^-, ICl_4^-, ClF_2^-, etc.

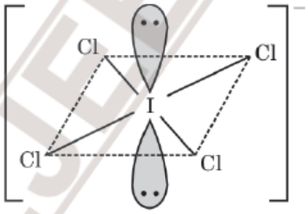
e.g. **ICl_4^-**

$V = 7, M = 4, C = 0, A = 1$

$$N = \frac{1}{2}[7 + 4 - 0 + 1] = 6$$

***sp*³*d*² hybridisation**

$L = 6 - 4 - 0 = 2$



Square planar

OBJECTIVE TYPE QUESTIONS

A Topicwise MULTIPLE CHOICE QUESTIONS *with only one correct answer*

Select the Correct Answers :

Chemical Bonds and Bond Polarity

A1. Which of the following molecules is not an exception to octet rule?

(*a*) BF_3 (*b*) PF_5 (*c*) CO_2 (*d*) IF_7.

A2. Which of the following has maximum covalent character?

(*a*) LiI (*b*) LiF (*c*) LiCl (*d*) LiBr.

A3. Which of the following has highest lattice energy

(*a*) LiF (*b*) NaF (*c*) KF (*d*) RbF.

A4. Which of the following molecule has net dipole moment ?

(*a*) CCl_4 (*b*) C_2H_2 (*c*) BF_3 (*d*) NH_3.

A5. The percentage ionic character of a bond having 1.275 Å its length and 1.03 D its dipole moment is :

(*a*) 10% (*b*) 15% (*c*) 16.83% (*d*) 18.8%.

A6. The correct order of dipole moment is

(*a*) $CH_4 < NF_3 < NH_3 < H_2O$

(*b*) $NF_3 < CH_4 < NH_3 < H_2O$

(*c*) $CH_4 < NH_3 < NF_3 < H_2O$

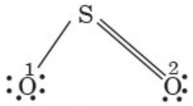
(*d*) $H_2O < NH_3 < NF_3 < CH_4$.

Answers

A1. (*c*) **A2.** (*a*) **A3.** (*a*) **A4.** (*d*) **A5.** (*c*) **A6.** (*a*)

Competition File

A7. Formal charge on two O atoms in



(*a*) –1, +1
(*b*) –1, 0
(*c*) 0, + 1
(*d*) –1, –1.

A8. Which of the following ion has maximum polarising power ?

(*a*) Na^+
(*b*) Mg^{2+}
(*c*) Ca^{2+}
(*d*) Al^{3+}

A9. Which of the following is not correct resonating structure for carbon dioxide ?

(*a*) $O = C = O$
(*b*) $^-O — C \equiv O^+$
(*c*) $^+O — C \equiv O^-$
(*d*) $^+O \equiv C — O^-$.

Shapes of Molecules

A10. The bond angles in molecules H_2O, NH_3, CH_4 and CO_2 are in the order :

(*a*) $H_2O > NH_3 > CH_4 > CO_2$
(*b*) $H_2O < NH_3 < CO_2 < CH_4$
(*c*) $H_2O < NH_3 < CH_4 < CO_2$
(*d*) $H_2O > NH_3 < CH_4 > CO_2$.

A11. The hybridisation of C involved in acetylene is :

(*a*) sp^2
(*b*) sp^3
(*c*) sp
(*d*) dsp^2.

A12. For which of the following hybridisation the bond angle is maximum ?

(*a*) sp^2
(*b*) sp
(*c*) sp^3
(*d*) dsp^2.

A13. The angle between covalent bonds is maximum in

(*a*) CH_4
(*b*) BF_3
(*c*) PF_3
(*d*) NH_3.

A14. The percentage *s*-character of the hybrid orbitals in methane, ethene and ethyne are

(*a*) 25, 50, 75
(*b*) 25, 33, 75
(*c*) 25, 33, 50
(*d*) 100, 50, 25.

A15. CO_2 is isostructural with

(*a*) $SnCl_2$
(*b*) $ZnCl_2$
(*c*) $HgCl_2$
(*d*) C_2H_4.

A16. In an octahedral structure, the pair of *d*-orbitals involved in d^2sp^3 hybridisation is ?

(*a*) $d_{x^2-y^2}, d_{xz}$
(*b*) d_{z^2}, d_{zx}
(*c*) d_{xy}, d_{yz}
(*d*) $d_{x^2-y^2}, d_{z^2}$

A17. Which of the following has highest bond angle ?

(*a*) NO_2^+
(*b*) NO_2
(*c*) NO_2
(*d*) NO_3.

A18. Which of the following molecules does not contain a lone pair of electrons ?

(*a*) NH_3
(*b*) PF_5
(*c*) H_2O
(*d*) SF_4

A19. In which of the following molecules, the central atom has two lone pairs of electrons ?

(*a*) SF_4
(*b*) BrF_5
(*c*) SO_2
(*d*) XeF_4

A20. What typs of hybridisation is possible in square planar molecules ?

(*a*) sp^3d
(*b*) dsp^3
(*c*) dsp^2
(*d*) sp^3d^2.

A21. PCl_5 molecule has the following geometry :

(*a*) Trigonal bipyramidal
(*b*) Octahedral
(*c*) Square plannar
(*d*) Plannar triangular.

A22. In which of the following molecules are all the bonds not equal ?

(*a*) BF_3
(*b*) AlF_3
(*c*) NF_3
(*d*) ClF_3

(*C.B.S.E. Med 2006*)

Molecular Orbital Theory

A23. Which of the following molecule/ion does not contain unpaired electrons ?

(*a*) N_2^+
(*b*) O_2^{2-}
(*c*) O_2
(*d*) B_2

A24. The calculated bond order in O_2^- ions is :

(*a*) 1
(*b*) 1½
(*c*) 2
(*d*) 2½

A25. If *z*–axis is considered as molecular axis, which of the following combinations is not possible for homonuclear diatomic molecules ?

(*a*) $2p_z + 2s$
(*b*) $2p_y - 2p_y$
(*c*) $2p_x + 2p_x$
(*d*) $2p_x + 2p_y$.

A26. Which of the following is paramagnetic ?

(*a*) O_2^-
(*b*) CN^-
(*c*) CO
(*d*) NO^+.

A27. Which one of the following pairs consists of only paramagnetic species ?

(*a*) O_2, NO
(*b*) O_2^+, O_2^{2-}
(*c*) CO, NO
(*d*) NO, NO^+

Answers

A7. (*b*) **A8.** (*d*) **A9.** (*c*) **A10.** (*c*) **A11.** (*c*) **A12.** (*b*) **A13.** (*b*) **A14.** (*c*) **A15.** (*c*) **A16.** (*d*)
A17. (*a*) **A18.** (*b*) **A19.** (*d*) **A20.** (*c*) **A21.** (*a*) **A22.** (*d*) **A23.** (*b*) **A24.** (*b*) **A25.** (*d*) **A26.** (*a*)
A27. (*a*)

Competition File

A28. The correct order of bond order values among the following is

(*i*) NO^- (*ii*) NO^+ (*iii*) NO (*iv*) NO^{2+} (*v*) NO^{2-}

(*a*) (*i*) < (*iv*) < (*iii*) < (*ii*) < (*v*)

(*b*) (*v*) = (*ii*) < (*i*) < (*iv*) < (*iii*)

(*c*) (*v*) < (*i*) < (*iv*) = (*iii*) < (*ii*)

(*d*) (*ii*) < (*iii*) < (*iv*) < (*i*) < (*v*)

A29. Which of the following is not paramagnetic ?

(*a*) O_2 (*b*) N_2^+

(*c*) B_2 (*d*) O_2^{2-}

A30. The bond strength is maximum in

(*a*) O_2^+ (*b*) O_2^-

(*c*) O_2 (*d*) O_2^{2-}

Hydrogen Bonding

A31. Hydrogen bond is strongest in

(*a*) S — H.....O (*b*) O — H.....S

(*c*) F — H.....F (*d*) F — H.....O

A32. The pair likely to form strongest hydrogen bonding is

(*a*) H_2O_2 and H_2O

(*b*) HCOOH amd CH_3COOH

(*c*) CH_3COOH and CH_3COOCH_3

(*d*) SiH_4 and $SiCl_4$

A33. Which of the following has highest boiling point?

(*a*) NH_3 (*b*) PH_3

(*c*) SbH_3 (*d*) AsH_3

A34. Which of the following has lowest boiling point?

(*a*) HF (*b*) HCl

(*c*) HI (*d*) HBr

A35. Which of the following statement is not true about water ?

(*a*) Water has more density than ice.

(*b*) Each water molecule is linked to four water molecules tetrahedrally

(*c*) In water, each O atom is bonded to 2-H atoms by hydrogen bonds.

(*d*) Water has minimum denisity at 277 K.

Answers

A28. (*c*) **A29.** (*d*) **A30.** (*a*) **A31.** (*c*) **A32.** (*b*) **A33.** (*a*) **A34.** (*b*) **A35.** (*d*)

B MULTIPLE CHOICE QUESTIONS *from Competitive Examinations*

AIPMT& Other State Boards' Medical Entrance

B1. The electronegativity difference between N and F is greater than that between N and H yet the dipole moment of NH_3 (1.5 D) is larger than that of NF_3 (0.2 D). This is because :

(*a*) in NH_3 the atomic dipole and bond dipole are in the same direction whereas in NF_3, these are in opposite directions.

(*b*) in NH_3 as well as NF_3 the atomic dipole and bond dipole are in opposite directions.

(*c*) in NH_3 the atomic dipole and bond dipole are in the opposite directions whereas in NF_3, these are in the same direction

(*d*) in NH_3 as well as in NF_3 the atomic dipole and bond dipole are in the same direction. *(C.B.S.E. Med 2006)*

B2. Which of the following is not a correct statement ?

(*a*) The canonical structures have no real existence.

(*b*) Every AB_5 molecule does in fact have square pyramid structure.

(*c*) Multiple bonds are always shorter than corresponding single bonds.

(*d*) The electron-deficient molecules can act as Lewis acids. *(C.B.S.E. Med 2006)*

B3. In which of the following pairs, the two species are isostructural :

(*a*) BrO_3^- and XeO_3

(*b*) SF_4 and XeF_4

(*c*) SO_3^{2-} and NO_3^-

(*d*) BF_3 and NF_3 *(C.B.S.E. Med. 2007)*

B4. The correct order of C—O bonds length among CO, CO_3^{2-}, and CO_2 is

(*a*) $CO < CO_2 < CO_3^{2-}$

(*b*) $CO_2 < CO_3^{2-} < CO$

(*c*) $CO < CO_3^{2-} < CO_2$

(*d*) $CO_3^{2-} < CO_2 < CO$. *(C.B.S.E.Med. 2007)*

B5. According to molecular orbital theory, which of the lists ranks the nitrogen species in terms of increasing bond order ?

(*a*) $N_2^{2-} < N_2^- < N_2$

(*b*) $N_2 < N_2^{2-} < N_2^-$

(*c*) $N_2^- < N_2^{2-} < N_2$

(*d*) $N_2^- < N_2 < N_2^{2-}$ *(C.B.S.E. PMT 2009)*

B6. In which of the following molecules/ions BF_3, NO_2^-, NH_2^- and H_2O, the central atom is sp^2 hybridised ?

(*a*) NH_2^- and H_2O (*b*) NO_2^- and H_2O

(*c*) BF_3 and NO_2^- (*d*) NO_2^- and NH_2^-

(C.B.S.E. PMT 2009)

Answers

B1. (*a*) **B2.** (*b*) **B3.** (*a*) **B4.** (*a*) **B5.** (*a*) **B6.** (*c*)

B7. In which one of the following species the central atom has the type of hybridization which is not the same as that present in the other three ?

(*a*) $SbCl_5^{2-}$ (*b*) PCl_5
(*c*) SF_4 (*d*) I_3^- *(C.B.S.E. Med. 2010)*

B8. Which one of the following species does not exist under normal conditions ?

(*a*) B_2 (*b*) Li_2
(*c*) Be_2^+ (*d*) Be_2 *(C.B.S.E. Med. 2010)*

B9. Among the following molecules : SO_2, SF_4, ClF_3, BrF_5 and XeF_4 which of the following shapes does not describe any of the molecules mentioned ?

(*a*) Bent (*b*) Trigonal bipyramidal
(*c*) See-saw (*d*) T-shape
(*e*) Square pyramidal *(Kerala PMT 2011)*

B10. Which of the following has the minimum bond length?

(*a*) O_2^+ (*b*) O_2^-
(*c*) O_2^{2-} (*d*) O_2 *(A.I.P.M.T. 2011)*

B11. Which of the two ions from the list given below have the geometry that is explained by the same hybridization of orbitals : NO_2^-, NO_3^-, NH_2^-, NH_4^+, SCN^- ?

(*a*) NO_2^- and NO_3^- (*b*) NH_4^+ and NO_3^-
(*c*) SCN^- and NH_2^- (*d*) NO_2^- and NH_2^-
(A.I.P.M.T. 2011)

B12. The pair of species with the same bond order is

(*a*) O_2^{2-}, B_2 (*b*) O_2^+, NO^+
(*c*) NO, CO (*d*) N_2, O_2 *(A.I.P.M.T. 2012)*

B13. Which of the following species contains three bond pairs and one lone pair around the central atom?

(*a*) H_2O (*b*) BF_3
(*c*) NH_2^- (*d*) PCl_3 *(A.I.P.M.T. 2012)*

B14. Which one of the following pairs is isostructural (*i.e.*, having the same shape and hybridization)?

(*a*) [BCl_3 and $BrCl_3$]
(*b*) [NH_3 and NO_3]
(*c*) [NF_3 and BF_3]
(*d*) [BF_4^- and NH_4^+] *(A.I.P.M.T. 2012)*

B15. Bond order of 1.5 is shown by

(*a*) O_2^+ (*b*) O_2^-
(*c*) O_2^{2-} (*d*) O_2 *(A.I.P.M.T. 2012)*

B16. Which of the following is a polar molecule ?

(*a*) SiF_4 (*b*) XeF_4
(*c*) BF_3 (*d*) SF_4
(NEET 2013)

B17. Which of the following is paramagnetic ?

(*a*) CN^- (*b*) NO^+
(*c*) CO (*d*) O_2^- *(NEET 2013)*

B18. Which one of the following molecules contains no π bond ?

(*a*) SO_2 (*b*) NO_2
(*c*) CO_2 (*d*) H_2O *(NEET 2013)*

B19. The bond orders for O_2^+ and C_2 respectively are

(*a*) 2.5, 2 (*b*) 3, 2
(*c*) 2, 2.5 (*d*) 2, 3
(*e*) 3, 3 *(Kerala PMT 2014)*

B20. Which of the following molecules has the maximum dipole moment ?

(*a*) CO_2 (*b*) CH_4
(*c*) NH_3 (*d*) NF_3 *(AIPMT 2014)*

B21. Which one of the following species has plane triangular shape ?

(*a*) N_3 (*b*) NO_3^-
(*c*) NO_2^- (*d*) CO_2 *(AIPMT 2014)*

B22. Which of the following sets of molecules contain the same number of lone pairs of electrons in the central atom?

(*a*) SO_2, ClF_3, BrF_3 (*b*) SF_4, NH_3, O_3
(*c*) ClF_3, XeF_2, H_2O (*d*) H_2O, SF_4, NH_3
(*e*) NH_3, XeF_2, O_3 *(Kerala PMT 2015)*

B23. Which one of the following does not match with respect to the shape of the molecule?

(*a*) NH_3 – Trigonal pyramidal
(*b*) SF_4 – Tetrahedral
(*c*) H_2S – Bent
(*d*) XeF_4 – Square planar *(AIPMT 2015)*

B24. Find the pair that has the same bond order with dimagnetic and paramagnetic properties respectively.

(*a*) F_2 and O_2 (*b*) N_2 and O_2^{2-}
(*c*) Li_2 and B_2 (*d*) B_2 and O_2
(e) He and Ne *(Kerala PMT 2015)*

B25. Decreasing order of stability of O_2, O_2^-, O_2^+ and O_2^{2-}

(*a*) $O_2 > O_2^+ > O_2^{2-} > O_2^-$
(*b*) $O_2^- > O_2^{2-} > O_2^+ > O_2$
(*c*) $O_2^+ > O_2 > O_2^- > O_2^{2-}$
(*d*) $O_2^{2-} > O_2^- > O_2 > O_2^+$ *(AIPMT 2015)*

B26. In which of the following pairs, both the species are not isostructural?

(*a*) NH_3, PH_3 (*b*) XeF_4, XeO_4
(*c*) $SiCl_4$, PCl_4^+ (*d*) diamond, silicon carbide
(AIPMT 2015)

Answers

B7. (*a*)	**B8.** (*d*)	**B9.** (*b*)	**B10.** (*a*)	**B11.** (*a*)	**B12.** (*a*)	**B13.** (*d*)	**B14.** (*d*)	**B15.** (*b*)	**B16.** (*d*)
B17. (*d*)	**B18.** (*d*)	**B19.** (*a*)	**B20.** (*c*)	**B21.** (*b*)	**B22.** (*b*)	**B23.** (*b*)	**B24.** (*c*)	**B25.** (*c*)	**B26.** (*b*)

Competition File

B27. Which of the following pairs of ions are isoelectronic and isostructural?

(*a*) SO_3^{2-}, NO_3^- (*b*) ClO_3^-, SO_3^{2-}

(*c*) CO_3^{2-}, SO_3^{2-} (*d*) ClO_3^-, CO_3^{2-}

(AIPMT 2015, 2016)

B28. The correct bond order in the following species is

(*a*) $O_2^+ < O_2^- < O_2^{2+}$ (*b*) $O_2^- < O_2^+ < O_2^{2+}$

(*c*) $O_2^{2+} < O_2^+ < O_2^-$ (*d*) $O_2^{2+} < O_2^- < O_2^+$

(AIPMT 2015)

B29. Maximum bond angle at nitrogen is present in which of the following?

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

(*c*) NO_2 (*d*) NO_2^- *(AIPMT 2015)*

B30. Consider the molecules CH_4, NH_3 and H_2O. Which of the given statement is false?

(*a*) The H—O—H bond angle in H_2O is smaller than the H—N—H bond angle in NH_3.

(*b*) The H—C—H bond angle in CH_4 is larger than the H—N—H bond angle in NH_3.

(*c*) The H—C—H bond angle in CH_4, the H—N—H bond angle in NH_3, and the H—O—H bond angle in H_2O are all greater than 90°.

(*d*) The H—O—H bond angle in H_2O is larger than the H—C—H bond angle in CH_4. *(NEET 2016)*

B31. Predict the correct order among the following:

(*a*) bond pair – bond pair > lone pair – bond pair > lone pair – lone pair

(*b*) lone pair – bond pair > bond pair – bond pair > lone pair – lone pair

(*c*) lone pair – lone pair > lone pair – bond pair > bond pair – bond pair

(*d*) lone pair – lone pair > bond pair – bond pair > lone pair – bond pair *(NEET 2016)*

B32. Which one of the following compound shows the presence of intramolecular hydrogen bond?

(*a*) H_2O_2 (*b*) HCN

(*c*) Cellulose (*d*) Concentrated acetic acid

(NEET 2016)

B33. The correct geometry and hybridization for XeF_4 are

(*a*) octahedral, sp^3d^2

(*b*) trigonal bipyramidal, sp^3d

(*c*) planar triangle, sp^3d^3

(*d*) square planar, sp^3d^2. *(NEET 2016)*

B34. The hybridizations of atomic orbitals of nitrogen in NO_2^+, NO_3^- and NH_4^+ respectively are

(*a*) sp, sp^3 and sp^2 (*b*) sp^2, sp^3 and sp^3

(*c*) sp, sp^2 and sp^3 (*d*) sp^2, sp and sp^3

(AIEEE 2011, NEET 2016)

B35. Which of the following pair of compounds is isoelectronic and isostructural?

(*a*) TeI_2, XeF_2 (*b*) IBr_2^-, XeF_2

(*c*) IF_3, XeF_2 (*d*) $BeCl_2$, XeF_2 *(NEET 2017)*

B36. The species, having bond angles of 120° is

(*a*) ClF_3 (*b*) NCl_3

(*c*) BCl_3 (*d*) PH_3 *(NEET 2017)*

B37. Which one of the following pair of species have the same bond order ?

(*a*) O_2, NO^+ (*b*) CN^-, CO

(*c*) N_2, O_2^- (*d*) CO, NO *(NEET 2017)*

B38. Among CaH_2, BeH_2, BaH_2, the order of ionic character is

(*a*) $BeH_2 < CaH_2 < BaH_2$

(*b*) $CaH_2 < BeH_2 < BaH_2$

(*c*) $BeH_2 < BaH_2 < CaH_2$

(*d*) $BaH_2 < BeH_2 < CaH_2$ *(NEET 2018)*

B39. Consider the following species: CN^+, CN^-, NO and CN. Which one of these will have the highest bond order ?

(*a*) NO (*b*) CN^-

(*c*) CN^+ (*d*) CN *(NEET 2018)*

B40. In the structure of ClF_3, the number of lone pairs of electrons on central 'Cl' atom is

(*a*) one (*b*) two

(*c*) four (*d*) three *(NEET 2018)*

JEE (Main) & Other State Boards' Engineering Entrance

B41. Which of the following molecules/ions do not contain unpaired electrons ?

(*a*) B_2 (*b*) N_2^+

(*c*) O_2 (*d*) O_2^{2-} *(A.I.E.E.E. 2006)*

B42. Which of the following hydrogen bonds is the strongest ?

(*a*) F—H.........F (*b*) O—H.........O

(*c*) O—H.........F (*d*) O—H.........N

(A.I.E.E.E. 2007)

B43. Which one of the following pairs of species have the same bond order ?

(*a*) NO^+ and CN^+ (*b*) CN^- and NO^+

(*c*) CN^- and CN^+ (*d*) O_2^- and CN^-

(A.I.E.E.E. 2008)

Answers

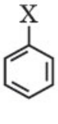
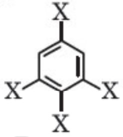
B27. (*b*) **B28.** (*b*) **B29.** (*a*) **B30.** (*d*) **B31.** (*c*) **B32.** (*c*) **B33.** (*d*) **B34.** (*c*) **B35.** (*b*) **B36.** (*c*)
B37. (*b*) **B38.** (*a*) **B39.** (*b*) **B40.** (*b*) **B41.** (*d*) **B42.** (*a*) **B43.** (*b*)

Competition File

B44. The types of hybridisation on the five carbon atoms from left to right in the molecule

$CH_3—CH=C=CH—CH_3$ are

(*a*) $sp^3, sp^2, sp^2, sp^2, sp^3$
(*b*) $sp^3, sp, sp^2, sp^2, sp^3$
(*c*) $sp^3, sp^2, sp, sp^2, sp^3$
(*d*) $sp^3, sp^2, sp^2, sp, sp^3$
(*e*) sp^3, sp, sp, sp^2, sp^3 *(Kerala P.E.T. 2009)*

B45. Dipole moment of  is 1.5 D. The dipole moment of  is (X = halogen)

(*a*) 1.5 D (*b*) 2.25 D
(*c*) 1 D (*d*) 3 D
(West Bengal JEE 2010)

B46. How many hydrogen bonded water molecule(s) are associated with $CuSO_4.5H_2O$?
(*a*) 1 (*b*) 2
(*c*) 3 (*d*) 4 *(AMU Engg. 2010, 2014)*

B47. Which one of the following conversions involve change in both hybridization and shape ?
(*a*) $CH_4 \rightarrow C_2H_6$ (*b*) $NH_3 \rightarrow NH_4^+$
(*c*) $BF_3 \rightarrow BF_4^-$ (*d*) $H_2O \rightarrow H_3O^+$
(Karnataka CET 2010)

B48. N_2 and O_2 are converted to monopositive cations N_2^+ and O_2^+ respectively. Which is incorrect ?
(*a*) In N_2^+ the N — N bond is weakened
(*b*) In O_2^+, the bond order increases
(*c*) In O_2^+, paramagnetism decreases
(*d*) N_2^+ becomes diamagnetic
(*e*) Both O_2 and O_2^+ are paramagnetic
(Kerala PET 2010)

B49. The structure of IF_7 is
(*a*) square pyramid (*b*) trigonal bipyramid
(*c*) octahedral (*d*) pentagonal bipyramid
(A.I.E.E.E. 2011)

B50. Likely bond angles of SF_4 molecule are
(*a*) 89°, 117° (*b*) 120°, 180°
(*c*) 45°, 118° (*d*) 117°, 92° *(A.I.E.E.E. 2011)*

B51. Which of the following has maximum number of lone pairs associated with Xe ?
(*a*) XeF_4 (*b*) XeF_6
(*c*) XeF_2 (*d*) XeO_3 *(A.I.E.E.E. 2011)*

B52. The number of types of bonds between two carbon atoms in calcium carbide is
(*a*) one sigma, one *pi*
(*b*) two sigma, one *pi*
(*c*) two sigma, two *pi*
(*d*) one sigma, two *pi* *(A.I.E.E.E. 2011)*

B53. The state of hybridization of the central atom and the number of lone pairs over the central atom in $POCl_3$ are
(*a*) *sp*,0 (*b*) sp^2, 0
(*c*) sp^3, 0 (*d*) dsp^2, 1 *(W.B.J.E.E. 2012)*

B54. The paramagnetic behaviour of B_2 is due to the presence of
(*a*) 2 unpaired electrons in π_b MO
(*b*) 2 unpaired electrons in π^* MO
(*c*) 2 unpaired electrons in σ^* MO
(*d*) 2 unpaired electrons in σ_b MO *(W.B.J.E.E. 2012)*

B55. Which one of the following contains ionic, covalent and co-ordinate bonds?
(*a*) NaOH (*b*) NaCl
(*c*) NaCN (*d*) NaNC
(Karnataka C.E.T. 2012)

B56. In which of the following pairs the two species are not isostructural?
(*a*) PCl_4^+ and $SiCl_4$ (*b*) PF_5 and BrF_5
(*c*) AlF_6^{3-} and SF_6 (*d*) CO_3^{2-} and NO_3^-
(A.I.E.E.E. 2012)

B57. The increasing order of O–N–O bond angle in the species NO_2, NO_2^+ and NO_2^- is
(*a*) $NO_2^+ < NO_2 < NO_2^-$
(*b*) $NO_2^- < NO_2 < NO_2^+$
(*c*) $NO_2^+ < NO_2^- < NO_2$
(*d*) $NO_2 < NO_2^+ < NO_2^-$
(C.B.S.E. PMT. 2008, W.B. JEE 2013)

B58. Molecular shapes of SF_4, CF_4 and XeF_4 and the number of lone pairs on the central atom are respectively.
(*a*) the same, with 1, 2 and 1
(*b*) the same, with 1, 0 and 1
(*c*) different, with 0, 1 and 2
(*d*) different, with 1, 0 and 2
(*e*) same, with 0, 0 and 1 *(Kerala P.E.T. 2013)*

B59. Allyl cyanide molecule contains
(*a*) 9 sigma bonds, 4 pi bonds and no lone pair
(*b*) 9 sigma bonds, 3 pi bonds and one lone pair
(*c*) 8 sigma bonds, 5 pi bonds and one lone pair
(*d*) 8 sigma bonds, 3 pi bonds and two lone pairs
(*e*) 6 sigma bonds, 2 pi bonds and four lone pairs
(Kerala P.E.T. 2013)

Answers

B44. (*c*) **B45.** (*a*) **B46.** (*a*) **B47.** (*c*) **B48.** (*d*) **B49.** (*d*) **B50.** (*a*) **B51.** (*c*) **B52.** (*d*) **B53.** (*c*)
B54. (*a*) **B55.** (*d*) **B56.** (*b*) **B57.** (*b*) **B58.** (*d*) **B59.** (*b*)

Competition File

B60. In which of the following pairs of molecules/ions, both the species are not likely to exist ?

(*a*) H_2^-, He_2^{2+} (*b*) H_2^+, He_2^{2-}

(*c*) H_2^-, He_2^{2-} (*d*) H_2^{2+}, He_2

(JEE Main 2013)

B61. Stability of the species Li_2, Li_2^- and Li_2^+ increases in the order of

(*a*) $Li_2^- < Li_2 < Li_2^+$

(*b*) $Li_2 < Li_2^+ < Li_2^-$

(*c*) $Li_2^- < Li_2^+ < Li_2$

(*d*) $Li_2 < Li_2^- < Li_2^+$ *(JEE Main 2013)*

B62. The structure of XeF_6 is experimentally determined to be distorted octahedron. Its structure according to VSEPR theory is

(*a*) octahedron

(*b*) trigonal bipyramid

(*c*) pentagonal bipyramid

(*d*) tetragonal bipyramid. *(W.B. JEE 2014)*

B63. 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. *(WB JEE 2014)*

B64. The lattice energy of NaCl is 788 kJ mol^{-1}. This means that 788 kJ of energy is required

(*a*) to separate one mole of solid NaCl into one mole of $Na^+(g)$ and one mole of $Cl^-(g)$ to infinite distance

(*b*) to separate one mole of solid NaCl into one mole of Na(*g*) and one mole of Cl(*g*) to infinite distance

(*c*) to convert one mole of solid NaCl into one mole of gaseous NaCl

(*d*) to convert one mole of gaseous NaCl into one mole of solid NaCl

(*e*) to separate one mole of gaseous NaCl into one mole $Na^+(g)$ and one mole of $Cl^-(g)$ to infinite distance.

(Kerala PET 2014)

B65. Molecular formulae and shapes of some molecules are given below. Choose the incorrect match.

Formula — **Shape**
(*a*) NH_3 — Trigonal pyramidal
(*b*) SF_4 — Tetrahedral
(*c*) ClF_3 — T-shaped
(*d*) PCl_5 — Trigonal bipyramidal
(*e*) BF_3 — Trigonal planar

(Kerala PET 2014)

B66. The pair of compounds having identical shapes for their molecules is

(*a*) CH_4, SF_4 (*b*) BCl_3, ClF_3

(*c*) XeF_2, $ZnCl_2$ (*d*) SO_2, CO_2

(Karnataka CET 2014)

B67. The correct arrangement of species in the decreasing order of the bond length between carbon and oxygen in them is

(*a*) CO, CO_2, HCO_2^-, CO_3^{2-}

(*b*) CO_2, HCO_2^-, CO, CO_3^{2-}

(*c*) CO_3^{2-}, HCO_2^-, CO_2, CO

(*d*) CO, CO_3^{2-}, CO_2, HCO_2^- *(Karnataka CET 2014)*

B68. Which one of the following properties is not shown by NO?

(*a*) Its bond order is 2.5.

(*b*) It is diamagnetic in gaseous state.

(*c*) It is a neutral oxide.

(*d*) It combines with oxygen to form nitrogen dioxide.

(JEE Main 2014)

B69. The number of lone pairs of electrons on the central atoms of H_2O, $SnCl_2$, PCl_3 and XeF_2 respectively, are

(*a*) 2, 1, 1, ,3 (*b*) 2, 2, 1, 3

(*c*) 3, 1, 1, 2 (*d*) 2, 1, 2, 3 *(WB JEE 2015)*

B70. The correct order of O—O bond length in O_2, H_2O_2 and O_3 is

(*a*) $O_2 > O_3 > H_2O_2$ (*b*) $H_2O_2 > O_3 > O_2$

(*c*) $O_3 > O_2 > H_2O_2$ (*d*) $O_3 > H_2O_2 > O_2$

(WB JEE 2016)

B71. Identify the T-shaped molecule in the following:

(*a*) BF_3 (*b*) NH_3

(*c*) NF_3 (*d*) ClF_3

(*e*) PCl_3 *(Kerala PET 2016)*

B72. Which one of the following molecule has the least dipole moment?

(*a*) H_2O (*b*) BeF_2

(*c*) NH_3 (*d*) NF_3

(*e*) PF_3 *(Kerala PET 2016)*

B73. Main axis of diatomic molecule is z-axis. The orbitals p_x and p_y overlap to form

(*a*) π-molecular orbital

(*b*) σ-molecular orbital

(*c*) δ-molecular orbital

(*d*) no bond is formed *(Karnataka CET 2016)*

B74. The increasing order of bond orders of O_2, O_2^+, O_2^- and O_2^{2-} is

(*a*) O_2^+, O_2, O_2^-, O_2^{2-} (*b*) O_2^{2-}, O_2^-, O_2^+, O_2

(*c*) O_2, O_2^+, O_2^-, O_2^{2-} (*d*) O_2^{2-}, O_2^-, O_2, O_2^+

(Karnataka CET 2016)

B75. The species in which the N atom in a state of *sp* hybridisation is

(*a*) NO_2^+ (*b*) NO_2^-

(*c*) NO_3^- (*d*) NO_2 *(JEE Main 2016)*

B76. The ground state magnetic property of B_2 and C_2 molecules will be

(*a*) B_2 paramagnetic and C_2 diamagnetic

(*b*) B_2 diamagnetic and C_2 paramagnetic

(*c*) both are diamagnetic

(*d*) both are paramagnetic. *(WB JEE 2017)*

Answers

B60. (*d*) **B61.** (*c*) **B62.** (*c*) **B63.** (*c*) **B64.** (*a*) **B65.** (*b*) **B66.** (*c*) **B67.** (*c*) **B68.** (*b*) **B69.** (*a*)
B70. (*b*) **B71.** (*d*) **B72.** (*b*) **B73.** (*d*) **B74.** (*d*) **B75.** (*a*) **B76.** (*a*)

Competition File

B77. Which of the following structures of a molecule is expected to have three bond pairs and one lone pair of electrons?
(*a*) Trigonal Planar (*b*) Tetrahedral
(*c*) Octahedral (*d*) Pyramidal
(Karnataka CET 2017)

B78. Which of the following is the correct electron dot structure of N_2O molecule?
(*a*) $:\ddot{N}{=}N{=}\underset{\cdot\cdot}{\ddot{O}}$ (*b*) $:\ddot{N}{-}\underset{+}{N}{=}\underset{\cdot\cdot}{\ddot{O}}:$
(*c*) $:N{=}N{=}\ddot{O}:$ (*d*) $:N{\equiv}N{-}\underset{\cdot\cdot}{\ddot{O}}:^-$
(Karnataka CET 2017)

B79. Among the following, the molecule that will have the highest dipole moment is
(*a*) H_2 (*b*) HI
(*c*) HBr (*d*) HCl
(*e*) HF *(Kerala PET 2017)*

B80. Which of the following pairs have identical bond order?
(*a*) CN^- and NO^+ (*b*) CN^- and O_2^-
(*c*) CN^- and CN^+ (*d*) NO^+ and O_2^-
(*e*) O_2^- and CN^+ *(Kerala PET 2017)*

B81. Which of the following species is not paramagnetic?
(*a*) NO (*b*) CO
(*c*) O_2 (*d*) B_2 *(JEE Main 2017)*

B82. What will be the geometry of the compound MB_4L_2? Here B is bond pair and L is lone pair.
(*a*) Square planar (*b*) Octahedral
(*c*) Square pyramid (*d*) Tetrahedral
(J.K. CET 2018)

B83. What is the hybridisation and geometry of the given species? The species are XeF_2 and ICl_2^-
(*a*) sp^3d and trigonal bipyramidal
(*b*) sp^3d^2 and square planar
(*c*) sp^3d and linear
(*d*) sp^3 and irregular tetrahedron *(J.K. CET 2018)*

B84. Which of the following has the strongest H-bond?
(*a*) O – H --- S (*b*) S – H --- O
(*c*) F – H --- F (*d*) F – H --- O
(W.B. JEE 2018)

B85. The intramolecular hydrogen bond is present in
(*a*) phenol (*b*) *o*-nitrophenol
(*c*) *p*-nitrophenol (*d*) *p*-cresol
(Karnataka CET 2018)

B86. The state of hybrid orbitals of carbon in CO_2, CH_4 and CO_3^{2-} respectively is
(*a*) sp^3, sp^2 and sp (*b*) sp^3, sp and sp^2
(*c*) sp, sp^3 and sp^2 (*d*) sp^2, sp^3 and sp.
(Karnataka CET 2018)

B87. According to molecular orbital theory, which of the following will not be a viable molecule ?
(*a*) He_2^{2+} (*b*) He^{2+}
(*c*) H_2^- (*d*) H_2^{2-} *(JEE Main 2018)*

B88. Which of the following compounds contain(s) no covalent bond(s)?
KCl, PH_3, O_2, B_2H_6, H_2SO_4
(*a*) KCl, B_2H_6, PH_3 (*b*) KCl, H_2SO_4
(*c*) KCl (*d*) KCl, B_2H_6
(JEE Main 2018)

B89. Total number of lone pair of electrons in I_3^- ion is:
(*a*) 3 (*b*) 6
(*c*) 9 (*d*) 12 *(JEE Main 2018)*

B90. According to molecular orbital theory, which of the following is true with respect to Li_2^+ and Li_2^- ?
(*a*) Both are unstable
(*b*) Li_2^+ is unstable and Li_2^- is stable
(*c*) Li_2^+ is stable and Li_2^- is unstable
(*d*) Both are stable *(JEE Main 2019)*

B91. In which of the following processes, the bond order has increased and paramagnetic character has changed to diamagnetic ?
(*a*) $N_2 \longrightarrow N_2^+$ (*b*) $NO \longrightarrow NO^+$
(*c*) $O_2 \longrightarrow O_2^{2-}$ (*d*) $O_2 \longrightarrow O_2^+$ *(JEE Main 2019)*

B92. Total pi and half sigma bonds are present in
(*a*) N_2^+ (*b*) N_2
(*c*) O_2^+ (*d*) O_2 *(JEE Main 2019)*

JEE (Advance) for IIT Entrance

B93. The hybridisation of atomic orbitals of nitrogen in NO_2^+, NO_3^- and NH_4^+ are
(*a*) sp, sp^3 and sp^2 respectively
(*b*) sp, sp^2 and sp^3 respectively
(*c*) sp^2, sp and sp^3 respectively
(*d*) sp^2, sp^3 and sp respectively.
(I.I.T. Screening 2000)

B94. Molecular shapes of SF_4, CF_4, and XeF_4 are
(*a*) the same with 2, 0 and 1 lone pairs of electrons respectively
(*b*) the same with 1, 1 and 1 lone pairs of electrons respectively
(*c*) different with 0, 1 and 2 lone pairs of electrons respectively
(*d*) different with 1, 0 and 2 lone pairs of electrons respectively. *(I.I.T. Screening 2000, AIEEE 2005, Kerala P.E.T. 2013)*

Answers

B77. (*d*) **B78.** (*d*) **B79.** (*e*) **B80.** (*a*) **B81.** (*b*) **B82.** (*a*) **B83.** (*c*) **B84.** (*c*) **B85.** (*b*) **B86.** (*c*)
B87. (*d*) **B88.** (*c*) **B89.** (*c*) **B90.** (*d*) **B91.** (*b*) **B92.** (*a*) **B93.** (*b*) **B94.** (*d*)

Competition File

B95. The correct order of hybridisation of the central atom in the following species : NH_3, $[PtCl_4]^{2-}$, PCl_5 and BCl_3 is

(*a*) dsp^2, dsp^3, sp^2 and sp^3

(*b*) sp^3, dsp^2, dsp^3, sp^2

(*c*) dsp^3, sp^2, sp^3, dsp^3

(*d*) dsp^2, sp^3, sp^2, dsp^3. *(I.I.T. Screening 2001)*

B96. Which of the following are isoelectronic and isostructural ?
NO_3^-, CO_3^{2-}, ClO_3^-, SO_3
(*a*) NO_3^-, CO_3^{2-}, (*b*) SO_3, NO_3^-,
(*c*) ClO_3^-, CO_3^{2-} (*d*) CO_3^{2-}, SO_3 *(I.I.T. 2003)*

B97. Total number of lone pair of electrons in $XeOF_4$ is ?
(*a*) 0 (*b*) 1
(*c*) 2 (d) 3 *(I.I.T. 2004)*

B98. Which species has the maximum number of lone pair of electrons on the central atom ?
(*a*) ClO_3^- (*b*) XeF_4
(*c*) SF_4 (*d*) $[I_3]^-$
(I.I.T. Screening 2005)

B99. The correct order of stability of the following resonance structures is

(I) $H_2C{=}N^+{=}N^-$
(II) $H_2C^+{-}N{=}N^-$
(III) $H_2C^-{-}N^+{\equiv}N$
(IV) $H_2C^-{-}N{=}N^+$
(*a*) I > II > IV > III (*b*) I > III > II > IV
(*c*) II > I > III > IV (*d*) III > I > IV > II
(I.I.T. JEE 2009)

B100. Assuming Hund's rule is violated, the bond order and magnetic nature of the diatomic molecule B_2 is
(*a*) 1 and diamagnetic
(*b*) 0 and diamagnetic
(*c*) 1 and paramagnetic
(*d*) 0 and paramagnetic *(I.I.T. 2010)*

B101. The species having pyramidal shape is :
(*a*) SO_3 (*b*) BrF_3
(*c*) SiO_3^{2-} (*d*) OSF_2 *(I.I.T. 2010)*

B102. The shape of XeO_2F_2 molecule is
(*a*) trigonal bipyramidal
(*b*) square planar
(*c*) tetrahedral
(*d*) see-saw *(I.I.T. J.E.E. 2012)*

Answers

B95. (*b*) **B96.** (*a*) **B97.** (*b*) **B98.** (*d*) **B99.** (*b*) **B100.** (*c*) **B101.** (*d*) **B102.** (*d*)

C MULTIPLE CHOICE QUESTIONS
with more than one correct answers

C1. Paramagnetic species are
(*a*) O_2^- (*b*) N_2
(*c*) C_2 (*d*) F_2

C2. The linear structure is possessed by
(*a*) $SnCl_2$ (*b*) CS_2
(*c*) NO_2^+ (*d*) SF_2

C3. Diamagnetic species are
(*a*) N_2 (*b*) O_2
(*c*) B_2 (*d*) O_2^{2-}

C4. Which of the following statements are not correct ?
(*a*) Hybrid orbitals form stronger bonds than *p*-orbitals.
(*b*) Promotion is essential for hybridisation.
(*c*) Boiling point of H_2O is more than H_2S.
(*d*) Resonance plays an important role in molecular orbital theory.

C5. In which of the following pairs, the shapes of the two molecules/ions is same ?
(*a*) H_2O, SF_2 (*b*) NH_3, SO_2
(*c*) PF_5, $SbCl_5$ (*d*) XeF_4, SF_4

C6. In which of the following pairs, both the molecules/ions involve same type of hybridisation for the central atom ?
(*a*) SF_6, XeF_6 (*b*) NH_3, H_2O
(*c*) ClF_3, PF_5 (*d*) IF_7, $XeOF_4$

C7. In which of the following, the geometry is not correctly given ?
(*a*) PH_3 : Trigonal pyramidal
(*b*) SiH_4 : Tetrahedral
(*c*) ClF_3 : Trigonal planar
(*d*) SF_4 : Square planar

C8. CO_2 is isostructural with
(*a*) $SnCl_2$ (*b*) SF_2
(*c*) $HgCl_2$ (*d*) C_2H_2

Answers

C1. (*a,c*) **C2.** (*b,c*) **C3.** (*a,d*) **C4.** (*b,d*) **C5.** (*a,c*) **C6.** (*b,c*) **C7.** (*c,d*) **C8.** (*c,d*)

C9. Hydrogen bonding plays a central role in the following phenomena :

(*a*) Ice floats in water.

(*b*) Higher Lewis basicity of primary amines than tertiary amines in aqueous solutions.

(*c*) Formic acid is more acidic than acetic acid.

(*d*) Dimerisation of acetic acid in benzene.

(*JEE Advance 2014*)

C10. The compound(s) with two lone pairs of electrons on the central atom is (are)

(*a*) BrF_5 (*b*) ClF_3

(*c*) XeF_4 (*d*) SF_4 (*JEE Advance 2016*)

C11. According to molecular orbital theory,

(*a*) C_2^{2-} is expected to be diamagnetic

(*b*) O_2^{2+} is expected to have a longer bond length than O_2

(*c*) N_2^+ and N_2^- have the same bond order

(*d*) He_2^+ has the same energy as two isolated He atom. (*JEE Advance 2016*)

C12. Which statements are correct for the peroxide ion?

(*a*) It has five completely filled anti-bonding molecular orbitals.

(*b*) It is diamagnetic.

(*c*) It has bond order one.

(*d*) It is isoelectronic with neon. (*W.B. JEE 2018*)

Answers

C9. (*a,b,d*) **C10.** (*b,c*) **C11.** (*a,c*) **C12.** (*b,c*)

D MULTIPLE CHOICE QUESTIONS

based on the given passage/comprehension

Passage I

In order to explain the characteristic geometrical shapes of polyatomic molecules, Pauling introduced the concept of hybridisation. The orbitals undergoing hybridisation should have nearly same energy. There are various types of hybridisations involving *s*, *p* and *d*-type of orbitals. The type of hybridisation gives the characteristic shape of the molecule or ion.

Answer the following questions :

D1. Which of the following statement is not correct ?

(*a*) The hybridised orbitals are always equivalent in energy and shape.

(*b*) *sp* hybridised orbitals has more *s*-character than sp^2 hybridised orbital.

(*c*) Promotion of electron is essential condition prior to hybridisation.

(*d*) The hybridized orbitals are directed in space in some preferred directions to have minimum repulsion between electron pairs.

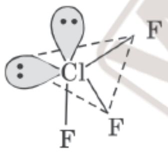
D2. Which other molecule or ion has same shape as NO_2^+ ion ?

(*a*) SF_2 (*b*) H_3O^+

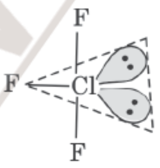
(*c*) XeF_2 (*d*) CO_3^{2-}

D3. Which of the following has correct placement of lone pairs and bond pairs ?

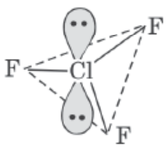
(*a*)



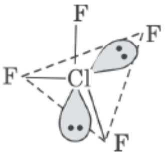
(*b*)



(*c*)



(*d*)



D4. Which molecule does not have the same type of hybridisation as P has in PF_5?

(*a*) ClF_3 (*b*) SF_4

(*c*) XeF_4 (*d*) XeF_2

D5. Which of the following molecule / ion does not have same number of lone pairs ?

(*a*) SF_4 (*b*) PH_3

(*c*) ClO_3^- (*d*) XeF_2

Passage II

Molecular orbital theory as developed by Hund and Mulliken concerns with the formation of molecular orbitals formed by linear combination of atomic orbitals. The electrons are present in these molecular orbitals. The molecular orbitals are filled exactly in the same way as atomic orbitals are filled. The molecular orbital configuration helps us to calculate bond order which gives information about the number of bonds present between atoms. The bond order is related to bond length and bond strength.

Answer the following questions :

D6. Which of the following combination does not give σ MO (assume Z-axis as internuclear axis)

(*a*) $2p_x + 2p_x$ (*b*) $2p_z + 2s$

(*c*) $2s + 2s$ (*d*) $2p_z + 2p_z$

D7. Which one of the following does not have single electron in a bonding molecular orbital?

(*a*) CN (*b*) B_2

(*c*) NO (*d*) N_2^+

D8. Which of the following MO has highest energy in a molecular orbital energy diagram or N_2 molecule?

(*a*) σ^*2s (*b*) $\sigma 2pz$

(*c*) $\pi 2px$ (*d*) $\sigma 2s$

Answers

Passage I. D1. (*c*) **D2.** (*c*) **D3.** (*b*) **D4.** (*c*) **D5.** (*d*)

Passage II. D6. (*a*) **D7.** (*c*) **D8.** (*b*)

Competition File

D9. Which of the following is expected to have largest bond length ?

(*a*) O_2 (*b*) O_2^+
(*c*) O_2^- (*d*) O_2^{2-}

D10. Which of the following will have maximum number of electrons in antibonding MOs ?

(*a*) N_2^+ (*b*) O_2^+
(*c*) F_2 (*d*) Be_2

Answers

Passage II. D9. (*d*) **D10.** (*c*)

Assertion Reason Type Questions

The questions given below consists of an Assertion and the Reason. Use the following key to choose the appropriate answer.

(*a*) If both assertion and reason are CORRECT and reason is the CORRECT explanation of the assertion.
(*b*) If both assertion and reason are CORRECT, but reason is NOT THE CORRECT explanation of the assertion.
(*c*) If assertion is CORRECT but reason is INCORRECT.
(*d*) If assertion is INCORRECT but reason is CORRECT.
(*e*) If both assertion and reason are INCORRECT.

1. Assertion : Ionic compounds tend to non-volatile.
Reason : The intermolecular forces in these compounds are weak.

2. Assertion : The dipole moment helps to predict whether a molecule is polar or non-polar.
Reason : The dipole moment helps to predict the geometry of molecules.

3. Assertion : BF_3 molecule is planar while NF_3 is pyramidal.
Reason : N atom is smaller than B atom.

4. Assertion : CO_2 is non-polar while H_2O is polar, though both are triatomic.
Reason : CO_2 is linear while H_2O is angular.

5. Assertion : NO_3^- is plannar while NH_3 is pyramidal.
Reason : N in NO_3^- has sp^2 and in NH_3 has sp^3 hybridisation.

6. Assertion : Both BF_3 and PF_5 do not obey octet rule.
Reason : Both are electron deficient molecules.

7. Assertion : Bond angle in H_2O is less than that in H_2S.
Reason : Electronegativity of O is more than that of S.

8. Assertion : C_2H_2 molecule is linear.
Reason : In C_2H_2 carbon atoms remain unhybridized.

9. Assertion : *cis* 1, 2-dichloroethane has no dipole moment.
Reason : Two C–Cl bonds cancel the bond polarity of each other.

10. Assertion : Covalent bonds are rigid and directional.
Reason : Covalent compounds undergo molecular reactions which are very slow.

11. Assertion : Though the central atoms of both NH_3 and H_2O molecules are sp^3 hydridised, yet H–N–H bond angle is greater than that of H–O–H.
Reason : This is because nitrogen atom has one lone pair and oxygen atom has two lone pairs.
(NCERT Exemplar Problem)

12. Assertion : Among two O–H bonds in H_2O molecule, the energy required to break the first O–H bond and the other O–H bond is the same.
Reason : This is because the electronic environment around oxygen is the same even after breakage of one O–H bond.
(NCERT Exemplar Problem)

Answers

1. (*c*) **2.** (*a*) **3.** (*b*) **4.** (*a*) **5.** (*a*) **6.** (*c*) **7.** (*d*) **8.** (c) **9.** (*e*) **10.** (*b*)
11. (*a*) **12.** (*e*)

Matching Type Questions

1. Match the orbital overlap figures shown in List-I with the description given in List-II and select the correct answer using the code given below the lists.

List-I	List-II
(P) 	**1.** *p* – *d*π antibonding
(Q) 	**2.** *d* – *d* σ bonding
(R) 	**3.** *p* – *d* π bonding
(S) 	**4.** *d* – *d* σ antibonding

Code:

	P	Q	R	S
(*a*)	2	1	3	4
(*b*)	4	3	2	1
(*c*)	2	3	1	4
(*d*)	4	1	3	2

(JEE Advance 2014)

Answers

1. (*c*)

Competition File

2. Match the interhalogen compounds of column-I with the geometry in column II and assign the correct code.

Column-I	Column-II
(P) XX'	(*i*) T-shape
(Q) XX'_3	(*ii*) Pentagonal bipyramidal
(R) XX'_5	(*iii*) Linear
(S) XX'_7	(*iv*) Square-pyramidal
	(*v*) Tetrahedral

Code:

	(P)	**(Q)**	**(R)**	**(S)**
(*a*)	(*iii*)	(*i*)	(*iv*)	(*ii*)
(*b*)	(*v*)	(*iv*)	(*iii*)	(*ii*)
(*c*)	(*iv*)	(*iii*)	(*ii*)	(*i*)
(*d*)	(*iii*)	(*iv*)	(*i*)	(*ii*)

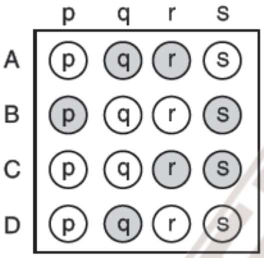
(*NEET 2017*)

Answers

2. (*a*)

Matrix Match Type Questions

Each question contains statements given in two columns, which have to be matched. Statements in Column I are labelled as A, B, C and D whereas statements in Column II are labelled as *p*, *q*, *r* and *s*. Match the entries of Column I with appropriate entries of Column II. Each entry in Column I may have one or more than one correct option from Column II. The answers to these questions have to be appropriately bubbled as illustrated in the following example.



	p	q	r	s
A	○	●	●	○
B	●	○	○	●
C	○	○	●	●
D	○	●	○	○

If the correct matches are A-*q*, A-*r*, B-*p*, B-*s*, C-*r*, C-*s* and D-*q*, then the correctly bubbled matrix will look like the following:

1. Match the molecule in Column I with the shape in Column II

Column I	Column II
(A) SF_4	(*p*) Pyramidal
(B) ClF_3	(*q*) Square planar
(C) XeF_4	(*r*) Sea saw
(D) NH_3	(*s*) T-shaped

2. Match the molecule in Column I with the characteristic in Column II

Column I	Column II
(A) O_2^-	(*p*) bond order 2.5 and paramagnetic
(B) N_2	(*q*) bond order 1.5 and paramagnetic
(C) N_2^+	(*r*) bond order 1 and paramagnetic
(D) B_2	(*s*) bond order 3 and diamagnetic

3. Match the molecule in Column I with the characteristic in Column II

Column I	Column II
(A) CO	(*p*) has one lone pair of electrons
(B) SF_4	(*q*) has longer bond length than its unipositive ion
(C) NH_3	(*r*) is paramagnetic
(D) O_2	(*s*) has dipole moment

4. Match the molecule in Column I with the characteristic in Column II

Column I	Column II
(A) B_2	(*p*) paramagnetic
(B) N_2	(*q*) undergoes oxidation
(C) O_2^-	(*r*) undergoes reduction
(D) O_2	(*s*) bond order ≥ 2
	(*t*) mixing of *s* and *p* orbitals

(*IIT-JEE 2009*)

5. Match the species in Column I with bond order in Column II.

Column I	Column II
(A) NO	(*p*) 1.5
(B) CO	(*q*) 2.0
(C) O_2^-	(*r*) 2.5
(D) O_2	(*s*) 3.0

6. Match the items given in Column I with examples given in Column II.

Column I	Column II
(A) Hydrogen bond	(*p*) C
(B) Resonance	(*q*) LiF
(C) Ionic solid	(*r*) HF
(D) Covalent solid	(*s*) O_3

Answers

1. : (A) – (*r*) (B) – (*s*) (C) – (*q*) (D) – (*p*)
2. (A) – (*q*) (B) – (*s*) (C) – (*p*) (D) – (*r*)
3. : (A) – (*q*), (*s*) (B) – (*p*) (C) – (*p*) (D) – (*q*), (*r*)
4. (A) – (*p*), (*r*), (*t*) (B) – (*s*), (*t*) (C) – (*p*), (*q*), (D) – (*p*), (*q*),(*s*)
5. : (A) – (*r*) (B) – (*s*) (C) – (*p*) (D) – (*q*)
6. (A) – (*r*), (B) – (*s*) (C) – (*q*) (D) – (*p*)

Competition File

Integer Type Questions

The answer to each of the following questions is a **single digit integer** ranging from 0 to 9.

1. The number of molecules or ions having bond order 2.5 among O_2^+, CN, NO, N_2^+, CO^+, NO^+, O_2^-, CN^-, N_2; is

2. Total number of molecular orbitals occupying one or two electrons in O_2^+ is

3. Total number of coordinate bonds present in $CuSO_4.5H_2O$ is

4. Total number of electrons present in πMOs in B_2 molecule is

5. The number of molecules having more than one lone pair among the following :
XeF_4, ClF_3, NH_3, SF_4, XeF_2, BrF_5, H_2O

6. Number of molecules having dipole moment among: BF_3, H_2O, NF_3, H_2S, CO_2, trans-1, 2-dichloroethene, CH_3Cl, CCl_4, HI is

7. The number of molecules in which all atoms donot obey octet rule among the following :
BeH_2, LiCl, PCl_3, SF_2, BF_3, IF_7, SO_2, XeF_2, PCl_5, H_2SO_4

8. $COCl_2$ is a poisonous gas. The formal charge on O atom is

9. The number of 90° bond angles present in SF_4 molecule is

10. Total number of lone pairs present in the structure of HNO_3 is

11. Based on VSEPR theory, the number of 90 degree F–B–F angles in BrF_5 is *(I.I.T. 2010)*

12. A list of species having the formula XZ_4 is given below:
XeF_4, SF_4, SiF_4, BF_4^-, BrF_4^-, $[Cu(NH_3)_4]^{2+}$, $[FeCl_4]^{2-}$, $[CoCl_4]^{2-}$ and $[PtCl_4]^{2-}$. Defining shape on the basis of the location of X and Z atoms, the total number of species having a square planar shape is *(JEE Advance 2014)*

13. Among the triatomic molecules/ions, $BeCl_2$, N_3^-, N_2O, NO_2^+, O_3, SCl_2, ICl_2^-, I_3^- and XeF_2, total number of linear molecule(s)/ion(s) where the hydridization of the central atom does not have contribution from the *d*-orbital(s) is [Atomic number : S = 16, Cl = 17, I = 53 and Xe = 54] *(JEE Advance 2015)*

14. Among H_2, He_2^+, Li_2, Be_2, B_2, C_2, N_2, O_2^- and F_2, the number of diamagnetic species is (Atomic numbers: H =1, He = 2, Li = 3, Be = 4, B = 5, C = 6, N = 7, O = 8, F = 9). *(JEE Advance 2017)*

15. The sum of the number of lone pairs of electrons on each central atom in the following species is
$[TeBr_6]^{2-}$, $[BrF_2]^+$, SNF_3, and $[XeF_3]^-$
(Atomic numbers: N = 7, F = 9, S = 16, Br = 35, Te = 52, Xe = 54). *(JEE Advance 2017)*

Answers

1. (4) **2.** (8) **3.** (4) **4.** (2) **5.** (4) **6.** (5) **7.** (6) **8.** (0) **9.** (0) **10.** (7)
11. (0) **12.** (4) **13.** (4) **14.** (6) **15.** (6)

NCERT Exemplar Problems

Objective Questions

Multiple Choice Questions (Type-I)

1. Isostructural species are those which have the same shape and hybridisation. 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 $NO_3^-]$

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

(*a*) CO_2 (*b*) HI
(*c*) H_2O (*d*) SO_2

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

(*a*) *sp*, sp^3 and sp^2 (*b*) *sp*, sp^2 and sp^3
(*c*) sp^2, *sp* and sp^3 (*d*) sp^2, sp^3 and *sp*

4. 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 H_2O, HF and NH_3 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

Answers

1. (*b*) **2.** (*c*) **3.** (*b*) **4.** (*b*)

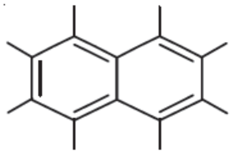
Competition File

5. In PO_4^{3-} ion the formal charge on the oxygen atom of P–O bond is
(*a*) + 1 (*b*) – 1
(*c*) – 0.75 (*d*) + 0.75

6. In NO_3^- ion, the number of bond pairs and lone pairs of electrons on nitrogen atom are
(*a*) 2, 2 (*b*) 3, 1
(*c*) 1, 3 (*d*) 4, 0

7. Which of the following species has tetrahedral geometry ?
(*a*) BH_4^- (*b*) NH_2^-
(*c*) CO_3^{2-} (*d*) H_3O^+

8. Number of π bonds and σ bonds in the following structure is :



(*a*) 6, 19 (*b*) 4, 20
(*c*) 5, 19 (*d*) 5, 20

9. Which of the following molecule/ion does not contain unpaired electrons ?
(*a*) N_2^+ (*b*) O_2
(*c*) O_2^{2-} (*d*) B_2

10. In which of the following molecule/ion all the bonds are not equal ?
(*a*) XeF_4 (*b*) BF_4^-
(*c*) C_2H_4 (*d*) SiF_4

11. In which of the following substances will hydrogen bond be strongest ?
(*a*) HCl (*b*) H_2O
(*c*) HI (*d*) H_2S

12. If the electronic configuration of an element is $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $3d^2$ $4s^2$, the four electrons involved in chemical bond formation will be __________.
(*a*) $3p^6$ (*b*) $3p^6, 4s^2$
(*c*) $3p^6, 3d^2$ (*d*) $3d^2, 4s^2$

13. Which of the following angle corresponds to sp^2 hybridisation ?
(*a*) 90° (*b*) 120°
(*c*) 180° (*d*) 109°

The electronic configurations of three elements, A, B and C are given below. Answer the questions 14 to 17 on the basis of these configurations.

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

14. Stable form of A may be represented by the formula :
(*a*) A (*b*) A_2
(*c*) A_3 (*d*) A_4

15. Stable form of C may be represented by the formula :
(*a*) C (*b*) C_2
(*c*) C_3 (*d*) C_4

16. The molecular formula of the compound formed from B and C will be
(*a*) BC (*b*) B_2C
(*c*) BC_2 (*d*) BC_3

17. The bond between B and C will be
(*a*) ionic (*b*) covalent
(*c*) hydrogen (*d*) coordinate

18. Which of the following order of energies of molecular orbitals of N_2 is correct ?
(*a*) $(\pi 2p_y) < (\sigma 2p_z) < (\pi^* 2p_x) \approx (\pi^* 2p_y)$
(*b*) $(\pi 2p_y) > (\sigma 2p_z) > (\pi^* 2p_x) \approx (\pi^* 2p_y)$
(*c*) $(\pi 2p_y) > (\sigma 2p_z) > (\pi^* 2p_x) \approx (\pi^* 2p_y)$
(*d*) $(\pi 2p_y) > (\sigma 2p_z) < (\pi^* 2p_x) \approx (\pi^* 2p_y)$

19. Which of the following statement is not correct from the view point of molecular orbital theory ?
(*a*) Be_2 is not a stable molecule.
(*b*) He_2 is not stable but He_2^+ is expected to exist.
(*c*) Bond strength of N_2 is maximum amongst the homonuclear diatomic molecules belonging to the second period.
(*d*) The order of energies of molecular orbitals in N_2 molecule is

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

20. Which of the following options represents the correct bond order :
(*a*) $O_2^- > O_2 > O_2^+$
(*b*) $O_2^- < O_2 < O_2^+$
(*c*) $O_2^- > O_2 < O_2^+$
(*d*) $O_2^- < O_2 > O_2^+$

21. The electronic configuration of the outermost shell of the most electronegative element is
(*a*) $2s^2 2p^5$ (*b*) $3s^2 3p^5$
(*c*) $4s^2 4p^5$ (*d*) $5s^2 5p^5$

22. Amongst the following elements whose electronic configurations are given below, the one having the highest ionisation enthalpy is
(*a*) $[Ne]3s^2 3p^1$ (*b*) $[Ne]3s^2 3p^3$
(*c*) $[Ne]3s^2 3p^2$ (*d*) $[Ar]3d^{10} 4s^2 4p^3$

Answers

5. (*c*) **6.** (*d*) **7.** (*a*) **8.** (*c*) **9.** (*c*) **10.** (*c*) **11.** (*b*) **12.** (*d*) **13.** (*b*) **14.** (*a*)
15. (*b*) **16.** (*d*) **17.** (*b*) **18.** (*a*) **19.** (*d*) **20.** (*b*) **21.** (*a*) **22.** (*b*)

Competition File

Multiple Choice Questions (Type-II)

23. Which of the following have identical bond order ?
(*a*) CN^- (*b*) NO^+
(*c*) $O_2{}^+$ (*d*) O_2^{2-}

24. Which of the following attain the linear structure :
(*a*) $BeCl_2$ (*b*) NCO^+
(*c*) NO_2 (*d*) CS_2

25. CO is isoelectronic with
(*a*) NO^+ (*b*) N_2
(*c*) $SnCl_2$ (*d*) NO_2^-

26. Which of the following species have the same shape ?
(*a*) CO_2 (*b*) CCl_4
(*c*) O_3 (*d*) NO_2^-

27. Which of the following statements are correct about CO_3^{2-} ?
(*a*) The hybridisation of central atom is sp^3.
(*b*) Its resonance structure has one C–O single bond and two C=O double bonds.
(*c*) The average formal charge on each oxygen atom is 0.67 units.
(*d*) All C–O bond lengths are equal.

28. Which among the following are diamagnetic ?
(*a*) N_2 (*b*) N_2^{2-}
(*c*) O_2 (*d*) O_2^{2-}

29. Species having same bond order are :
(*a*) N_2 (*b*) N_2^-
(*c*) F_2^+ (*d*) O_2^-

30. Which of the following statements are not correct ?
(*a*) NaCl being an ionic compound is a good conductor of electricity in the solid state.
(*b*) In canonical structures, there is a difference in the arrangement of atoms.
(*c*) Hybrid orbitals form stronger bonds than pure orbitals.
(*d*) VSEPR theory can explain the square planar geometry of XeF_4.

Answers

23. (*a*, *b*) **24.** (*a*, *d*) **25.** (*a*, *b*) **26.** (*c*, *d*) **27.** (*c*, *d*) **28.** (*a*, *d*) **29.** (*c*, *d*) **30.** (*a*, *b*)

Matching Type Questions

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

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

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

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

33. Match the species in Column I with the bond order in Column II.

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

34. Match the items given in Column I with examples given in Column II.

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

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

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

Answers

31. (*i*) – (*c*); (*ii*) – (*a*); (*iii*) – (*e*); (*iv*) – (*d*)
32. (*i*) – (*e*); (*ii*) – (*a*); (*iii*) – (*b*); (*iv*) – (*c*)
33. (*i*) – (*c*); (*ii*) – (*d*); (*iii*) – (*a*); (*iv*) – (*b*)
34. (*i*) – (*d*); (*ii*) – (*e*); (*iii*) – (*b*); (*iv*) – (*a*)
35. (*i*) – (*c*); (*ii*) – (*a*); (*iii*) – (*b*)

Competition File

Assertion and Reason Type Questions

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

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

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

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

(*d*) A and R both are false.

36. 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.

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

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

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

Answers

36. (*a*) **37.** (*a*) **38.** (*d*)

MCQ Based on Given Comprehension

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

Molecular orbitals are formed by the overlap of atomic orbitals. Two atomic orbitals combine to form two molecular orbitals called bonding molecular orbital (BMO) and anti-bonding molecular orbital (ABMO). Energy of anti-bonding orbital is raised above the parent atomic orbitals that have combined and the energy of the bonding orbital is lowered than the parent atomic orbitals. Energies of various molecular orbitals for elements hydrogen to nitrogen increase in the order : $\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < (\pi 2p_x \approx \pi 2p_y) < \sigma 2p_z < (\pi^* 2p_x \approx \pi^* 2p_y) < \sigma^* 2p_z$ and for oxygen and fluorine order of energy of molecular orbitals is given as : $\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \sigma 2p_z < (\pi 2p_x \simeq \pi 2p_y) < (\pi^* 2p_x \simeq \pi^* 2p_y) < \sigma^* 2p_z$. Different atomic orbitals of one atom combine with those atomic orbitals of the second atom which have comparable energies and proper orientation. Further, if the overlapping is head on, the molecular orbital is called '*pi*', (π). The molecular orbitals are filled with electrons according to the same rules as followed for filling of atomic orbitals. However, the order for filling is not the same for all molecules or their ions. Bond order is one of the most important parameters to compare the strength of bonds.

39. Which of the following statements is correct ?

(*a*) In the formation of dioxygen from oxygen atoms 10 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 same as total number of anti-bonding orbitals in dioxygen.

(*d*) Number of filled bonding orbitals will be same as number of filled anti-bonding orbitals.

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

(*a*) $\sigma^* 1s$ (*b*) $\sigma^* 2p_z$

(*c*) $\pi 2p_x$ (*d*) $\pi^* 2p_y$

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

(*a*) O_2, N_2 (*b*) O_2^+, N_2^-

(*c*) O_2^-, N_2^+ (*d*) O_2^-, N_2^-

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

(*a*) O_2 (*b*) Ne_2

(*c*) N_2 (*d*) F_2

Answers

39. (*a*) **40.** (*d*) **41.** (*b*) **42.** (*c*)

Competition File

Hints & Explanations for Difficult Objective Type Questions

A. mcq with only one correct answer

A3. (*a*): Because of small size of Li^+.

A5. (*c*): $\mu_{ionic} = q \times d$

$= 4.8 \times 10^{-10}$ e.s.u. $\times 1.275 \times 10^{-8}$ cm

$= 6.12 \times 10^{-18}$ e.s.u. cm = 6.12 D

% Ionic character

$$= \frac{\text{Observed dipole moment}}{\text{Dipole moment for complete ionic character}} \times 100$$

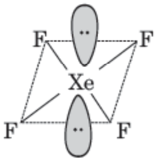
$$= \frac{1.03}{6.12} \times 100 = 16.83\%$$

A8. (*d*): Al^{3+} has maximum polarising power because of small size and high charge.

A10. (*c*): Bond angles are H_2O (104.5°), NH_3 (107°), CH_4 (109.5°) and CO_2 (180°).

A17. (*a*): NO_2^+ has linear geometry and therefore bond angle is highest (180°).

A19. (*d*): In XeF_4, there are two lone pairs.



A24. (*b*): O_2^- : KK $(\sigma 2s)^2(\sigma^* 2s)^2(\sigma 2p_z)^2(\pi 2p_x)^2(\pi 2p_y)^2(\pi^* 2p_x)^2$ $(\pi^* 2p_y)^1$

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

A28. (*c*): NO : $KK(\sigma_{2s})^2 (\sigma^*_{2s})^2 \ (\pi_{2p_x})^2 (\pi_{2p_y})^2 (\sigma_{2p_z})^2 (\pi^*_{2p_x})^1$

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

(*i*) B.O. $(NO^-) = \frac{8-4}{2} = 2$

(*ii*) B.O. $(NO^+) = \frac{8-2}{3} = 3$

(*iii*) B.O. (NO) = 2.5

(*iv*) B.O. $(NO^{2+}) = \frac{7-2}{2} = 2.5$

(*v*) B.O. $(NO^{2-}) = \frac{8-5}{2} = 1.5$

∴ Correct order is : (*v*) < (*i*) < (*iv*) = (*iii*) < (*ii*)

A29. (*d*): Only O_2^{2-} has all electrons paired and is diamagnetic. All other are paramagnetic.

A30. (*a*): Bond orders are O_2^+ (2.5), O_2 (2.0), O_2^- (1.5) and O_2^{2-} (1.0). So, O_2^+ has maximum bond strength.

A34. (*b*): HCl has lowest boiling point.

A35. (*d*): Water has maximum density at 277K.

B. mcq from competitive examinations

B2. (*b*) : AB_5 molecules may have square pyramidal or trigonal bipyramidal geometry.

B3. (*a*): Both BrO_3^- and XeO_3 involve sp^3 hybridisation of central atom and has one lone pair of electrons. These have pyramidal shape.

B4. (*a*): The correct order of CO bond length will be

$CO < CO_2 < CO_3^{2-}$

B6. (*c*): BF_3: sp^2, NO_2^-:sp^2, NH_2^-:sp^3, H_2O:sp^3

B7. (*a*): $SbCl_5^{2-}$ is sp^3d^2 while all other molecules/ions in the question involve sp^3d hybridisation.

B8. (*d*) : Bond order of Be_2 is zero, so it does not exist.

B9. (*b*) Shapes are : SO_2(angular), SF_4(see saw), ClF_3(T-shaped), BrF_5(square pyramidal), XeF_4(square planar).

B10. (*a*) : Bond order of O_2^+ is maximum 2.5 and hence minimum bond length.

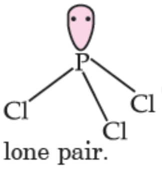
B11. (*a*) : The hybridizations are :

NO_2^- (sp^2), NO_3^- (sp^2), NH_2^- (sp^3), NH_4^+ (sp^3) $SCN^-$$(sp)$.

NO_2^- and NO_3^- have same hybridisation.

B12. (*a*) : O_2^{2-} and B_2 have bond order equal to 1.

B13. (*d*) :

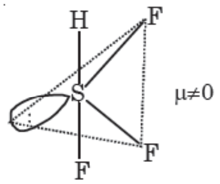


contains three bond pairs and one lone pair.

B14. (*d*) : BF_4^- and NH_4^+ involve sp^3 hybridisation and are tetrahedral.

B15. (*b*) : O_2^- : KK $(\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2(\pi 2p_x)^2(\pi 2p_y)^2(\pi^* 2p_x)^2$ $(\pi^* 2p_y)^1$; Bond order = $\frac{8-5}{2} = 1.5$ pyramidal.

B16. (*d*) : SF_4 has see saw shape involving sp^3d hybridisation. It has four bond pairs and one lone pair.



B17. (*d*) : O_2^- : $KK(\sigma 2s)^2 \ (\sigma^* 2s)^2 \ (\sigma 2p_z)^2(\pi 2p_x)^2(\pi 2p_y)^2$ $(\pi^* 2p_x)^2(\pi^* 2p_y)^1$

It has one unpaired electron and hence is paramagnetic.

Competition File

B18. (*d*) : H_2O does not contain any π bond.

B21. (*b*) : NO_3^- has plane triangular shape.

B22. (*b*) : SF_4, NH_3 and O_3 have one lone pair of electrons on the central atom.

B23. (*b*) : SF_4 has see saw shape and not tetrahedral.

B24. (*c*) :

Species	Bond order	Magnetic character
F_2	1	Diamagnetic
O_2	2	Paramagnetic
N_2	3	Diamagnetic
O_2^{2-}	1	Diamagnetic
Li_2	1	Diamagnetic
B_2	1	Paramagnetic

He and Ne are monoatomic and diamagnetic.

So, Li_2 and B_2 have same bond order, and diamagnetic and paramagnetic properties.

B25. (*c*) : The bond order of the species are:

$O_2^+ (2.5) > O_2 (2) > O_2^- (1.5) > O_2^{2-} (1)$

Thus, the order of stability is same as above.

B26. (*b*) : XeF_4 has square planar geometry and XeO_4 has tetrahedral geometry.

B27. (*b*) : SO_3^{2-} and ClO_3^- have same number of electrons (42) and same pyramidal shape.

B28. (*b*) : $O_2^- (1.5) < O_2^+ (2.5) < O_2^{2+} (3.0)$

B29. (*a*) : NO_2^+ is linear and bond angle of 180°.

B30. (*d*) : Bond angles in CH_4, NH_3 and H_2O are:

$CH_4 = 109.5°$, $NH_3 = 107°$ and $H_2O = 104.5°$

Statement (*d*) is wrong because bond angle of H_2O is smaller than that of NH_3.

B33. (*d*) : In XeF_4, the hybridisation is sp^3d^2 and geometry is square planar with two positions occupied by lone pairs.

B35. (*b*) : IBr_2^- and XeF_2 are isostructural (linear shape) and central atoms (I^- and Xe) of both contain same number of valence electrons.

B36. (*c*) : BCl_3 has trigonal planar structure and bond angle is 120°.

B37. (*b*) : CN^- and CO have same bond order of 3.

B38. (*a*) : Smaller the size of cation, more will be its polarising power. Hence, BeH_2 is least ionic.

$$BeH_2 < CaH_2 < BaH_2$$

B39. (*b*) : NO: KK $(\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p_x)^2$

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

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

$$CN^- : KK(\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p_x)^2 = (\pi 2p_y)^2(\sigma 2p_z)^2$$

$$\text{B.O.} = \frac{8-2}{2} = 3$$

$$CN : KK(\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p_x)^2 = (\pi 2p_y)^2(\sigma 2p_z)^1$$

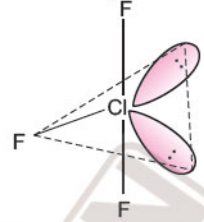
$$\text{B.O.} = \frac{7-2}{2} = 2.5$$

$$CN^+ : KK(\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p_x)^2 = (\pi 2p_y)^2$$

$$\text{B.O.} = \frac{6-2}{2} = 2$$

Hence CN^- has highest bond order.

B40. (*b*) : ClF_3 has two lone pairs of electrons on Cl atom.



B41. (*d*) : O_2^{2-} is diamagnetic.

B42. (*a*) : F—H.........F is the strongest hydrogen bond because of largest electronegativity difference between H and F.

B43. (*b*): NO^+ and CN^- are isoelectronic and have same bond order of 3.

B45. (*a*): The bond moments para to each other cancel due to their opposite directions. The other two groups are meta to each other at an angle of 120°.

∴ Dipole moment, $\mu = \sqrt{\mu_2^1 + \mu_2^2 + 2\mu_1\mu_2 \cos\theta}$

where $\mu_1 = \mu_2 = 1.5$ D

$$\therefore \quad \mu = \sqrt{(1.5)^2 + (1.5)^2 + 2(1.5)(1.5)\cos 120°} = 1.5 \text{ D}$$

B47. (*c*) : In BF_3, hybridisation of B is sp^2 and its geometry is trigonal planar. In BF_4^-, the hybridisation of B is sp^3 and its geometry is tetrahedral.

B51. (*c*) : No. of lone pairs : XeF_4(2), XeF_6(1), XeO_3(1), XeF_2(3).

B52. (*d*) : Calcium carbide is an ionic carbide having the structure :

$$Ca^{2+}(C \equiv C)^{2-}$$

It contains one sigma and two *pi* bonds.

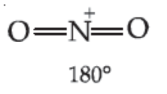
B53. (*c*) : In $POCl_3$, the hybridization is sp^3 and number of lone pair = 0

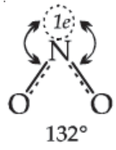
B54. (*a*) : B_2 : KK $(\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x)^1 (\pi 2p_y)^1$

B56. (*b*) : PF_5 is trigonal bipyramidal and BrF_5 is square

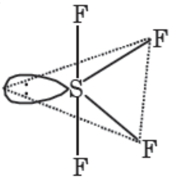
B57. (*b*) : NO_2^+ is linear molecule having bond angle of 180°.

NO_2 has one unshared electron while NO_2^- has a lone pair of electrons. Therefore, lone pair causes more repulsion than unshared electron and therefore, bond angle is forced closer.

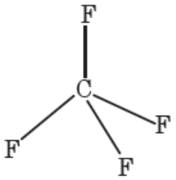




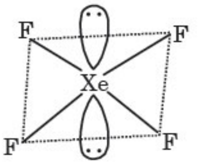
B58. (*d*) :



(lone pair = 1)

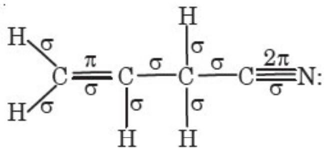


(lone pair = 0)



(lone pair = 2)

Hence, all have different shapes with 1, 0 and 2 lone pairs.

B59. (*b*) :


Allyl cyanide

σ = 9, π = 3, lone pair = 1.

B60. (*d*) : H_2^{2+} : $(\sigma 1s)^0$

Bond order = 0

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

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

Hence, He_2^{2+} and He_2 have zero bond order.

B61. (*c*) : Stability depends upon bond order.

Li_2 : $KK(\sigma 2s)^2$: Bond order = 1

Li_2^+ : $KK(\sigma 2s)^1$: Bond order = $\frac{1}{2}$

Li_2^- : $KK(\sigma 2s)^2(\sigma^* 2s)^1$: Bond order = $\frac{1}{2}$

Li_2^+ is more stable than Li_2^- because it has less number of antibonding electrons. Hence,

$$Li_2^- < Li_2^+ < Li_2$$

B63. (*c*) : The position of bond pairs of electrons in N–F bond is away from N than the position of bond pairs in N–H bonds. Therefore, the force of repulsion between the bonded pairs of electrons in NF_3 is less than that in NH_3. Hence, the larger lone pair-bond pair repulsion forces the bonded electron pairs to come closer to each other in NF_3 and bond angle is less in comparison to that in NH_3.

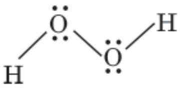
B65. (*b*) SF_4 has see-saw (distorted trigonal bipyramidal) shape.

B66. (*c*) Both XeF_2 and $ZnCl_2$ are linear molecules.

B68. (*b*) NO is paramagnetic in gaseous state due to presence of one unpaired electron.

B69. (*a*) H_2O : *l*.p = 2, $SnCl_2$: *l*.p. = 1,

PCl_3 : *l*.p. = 1, XeF_2 : *l*.p. = 3

B70. (*b*) H_2O_2 :


Bond order = 1

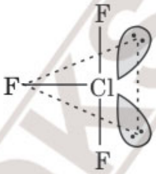
O_2 : $:\ddot{O}=\ddot{O}:$ Bond order = 2

O_3 :


Bond order between 1 and 2; approximately 1.5

∴ Bond length is $H_2O_2 > O_3 > O_2$

B71. (*d*) ClF_3 has T-shape



B72. (*b*) $F \rightleftarrows Be \rightleftarrows F$. The opposite bond dipoles cancel each other and the resulting dipole moment is zero.

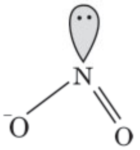
B73. (*d*) Bond orders are :

O_2^{2-} (1), O_2^- (1.5), O_2 (2), O_2^+ (2.5)

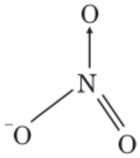
B75. (*a*)

$O=\overset{+}{N}=O$

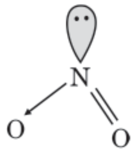
sp (NO_2^+)



sp^2 (NO_2^-)



sp^2 (NO_3^-)



sp^2 (NO_2)

N in NO_2^+ is *sp* hybridised.

B76. (*a*): B_2 : $KK(\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p_x)^1 = (\pi 2p_y)^1$

Two unpaired electrons and hence paramagnetic.

C_2 : $KK(\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p_x)^2 = (\pi 2p_y)^2$

No unpaired electron and hence diamagnetic.

B77. (*d*): A molecule with 3 bond pairs and 1 lone pair of electrons like NH_3 is pyramidal.

B78. (*d*): $:N\equiv\overset{+}{N}-\ddot{\underset{\cdot\cdot}{O}}:^-$ is the correct electron dot structure.

B80. (*a*): CN^- : $KK(\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p_x)^2 = (\pi 2p_y)^2(\sigma 2p_z)^2$

$$B.O. = \frac{8-2}{2} = 3$$

NO^+ : $KK(\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p_x)^2 = (\pi 2p_y)^2(\sigma 2p_z)^2$

$$B.O. = \frac{8-2}{2} = 3$$

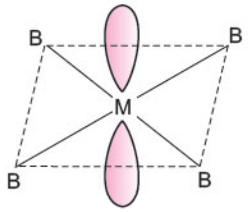
O_2^- : $KK(\sigma 2s)^2(\sigma^* 2s)^2(\sigma 2p_z)^2(\pi 2p_x)^2(\pi 2p_y)^2(\pi^* 2p_x)^2$ $(\pi^* 2p_y)^1$

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

CN^- and NO^+ have same bond order.

B81. (*b*): CO is diamagnetic while all other : O_2, B_2 and NO are paramagnetic.

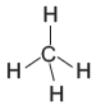
B82. (*a*): The structure will be octahedral with two lone pairs.



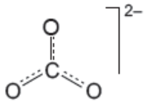
The geometry is square planar.

B86. (*c*):

O=C=O
sp hybridisation



sp^3 hybridisation



sp^2 hybridisation

B87. (*d*):

He_2^{2+} $(\sigma 1s)^2$ $\text{B.O.} = \frac{2-0}{2} = 1$

He_2^{+} $(\sigma 1s)^2(\sigma * 1s)^1$ $\text{B.O.} = \frac{2-1}{2} = 0.5$

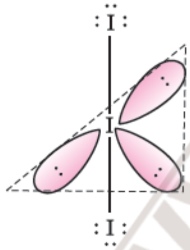
H_2^{-} $(\sigma 1s)^2(\sigma * 1s)^1$ $\text{B.O.} = \frac{2-1}{2} = 0.5$

H_2^{2-} $(\sigma 1s)^2(\sigma * 1s)^2$ $\text{B.O.} = \frac{2-2}{2} = 0$

H_2^{2-} is not viable molecule because bond order is zero.

B88. (*c*): KCl has only ionic bond.

B89. (*c*):



No. of lone pairs = 9

B90. (*d*): $Li_2 : (\sigma 1s)^2(\sigma^* 1s)^2(\sigma 2s)^2$

$Li_2^+ : (\sigma 1s)^2(\sigma^* 1s)^2(\sigma 2s)^1$

$\text{Bond order} = \frac{3-2}{2} = \frac{1}{2}$

$Li_2^- : (\sigma 1s)^2(\sigma^* 1s)^2(\sigma 2s)^2(\sigma^* 2s)^1$

$\text{Bond order} = \frac{4-3}{2} = \frac{1}{2}$

Both have bond order of 0.5 and are stable.

B91. (*b*):

(*a*) $N_2 \longrightarrow N_2^+$ B.O : 3 ⟶ 2.5; Dia ⟶ Para

(*b*) $NO \longrightarrow NO^+$ B.O : 2.5 ⟶ 3; Para ⟶ Dia

(*c*) $O_2 \longrightarrow O_2^-$ B.O : 2 ⟶ 1; Para ⟶ Dia

(*d*) $O_2 \longrightarrow O_2^+$ B.O : 2 ⟶ 2.5; Para ⟶ Para

B92. (*a*):

(*a*) $N_2^+ : (KK)(\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p_x)^2(\pi 2p_y)^2(\sigma 2p_z)^1$

$\text{B.O} = \frac{7-2}{2} = 2.5,\ 2\pi \text{ and } \frac{1}{2}\sigma$

(*b*) $N_2 : (KK)(\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p_x)^2(\pi 2p_y)^2(\sigma 2p_z)^2$

$\text{B.O} = \frac{8-2}{2} = 3;\ 2\pi \text{ and } 1\sigma$

(*c*) $O_2 : KK(\sigma 2s)^2(\sigma^* 2s)^2(\sigma 2p_z)^2(\pi 2p_x)^2(\pi 2p_y)^2(\pi^* 2p_x)^1$ $(\pi^* 2p_y)^1$

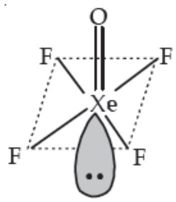
$\text{B.O} = \frac{8-4}{2} = 2;\ 1\pi \text{ and } 1\sigma$

(*d*) $O_2^+ : KK(\sigma 2s)^2(\sigma^* 2s)^2(\sigma 2p_z)^2(\pi 2p_x)^2(\pi 2p_y)^2(\pi^* 2p_x)^1$

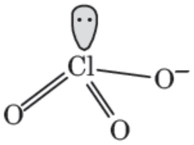
$\text{B.O} = \frac{8-4}{2} = 2;\ 1\pi \text{ and } 1\sigma$

B96. (*a*): NO_3^-: trigonal planar, CO_3^{2-} : trigonal planar, ClO_3^-: pyramidal and SO_3: trigonal planar. NO_3^- and CO_3^{2-} are isoelectronic also.

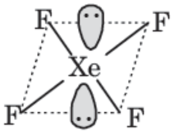
B97. (*b*): $XeOF_4$ involves sp^3d^2 hybridisation and has one lone pair of electrons.



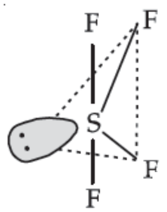
B98. (*d*): I_3^- has maximum number of unpaired electrons.



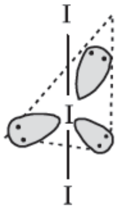
(*a*)



(*b*)



(*c*)



(*d*)

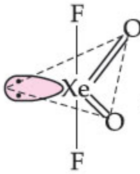
B100. (*c*) : B_2 (10) : $\sigma_{1s}^2\ \sigma_{1s}^{*2}\ \sigma_{2s}^2\ \sigma_{2s}^{*2}\ \pi 2p_x^{\ 1}\pi 2p_y^{\ 1}$

$\text{Bond order} = \frac{6-4}{2} = 1$

It is paramagnetic.

Competition File

B102. (*d*) : XeO_2F_2 involves sp^3d hybridisation and shape is



see saw.

C. mcq with more than one correct answer

C1.(*a,c*) : O_2^- and B_2 are paramagnetic while N_2 and F_2 are diamagnetic.

C2.(*b,c*) : $SnCl_2$ and SF_2 have an gular (or V) shape.

C3.(*a,d*) : B_2 and O_2 are paramagnetic.

C4.(*b,d*) : Promotion is not essential for hybridiation. Resonance has no role in M.O. theory.

C6.(*b,c*) : NH_3 and H_2O involve sp^3 hybridisation.

ClF_3 and PF_5 involve sp^3d hybridisation.

C7.(*c,d*) : ClF_3: T-shape, SF_4 : sea-saw

C9.(*a, b, d*) (*c*) is not correct because HCOOH is stronger acid than CH_3COOH due to inductive effect and not due to hydrogen bonding. All other are correct.

C11.(*a,c*) :(*a*) The M.O. electronic configuration of C_2^{2-} is

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

It is diamagnetic because there is no unpaired electron.

(*b*) Bond order of O_2^{2+} is 3 and that of O_2 is 2. therefore, bond length of O_2^{2+} is shorter than that of O_2.

(*c*) $N_2^+ : (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x)^2 = (\pi 2p_y)^2 (\sigma 2p_z)^1$

$$\text{Bond order of } N_2^+ = \frac{9-4}{2} = 2.5$$

$N_2^- : (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x)^2 = (\pi 2p_y)^2 (\sigma 2p_z)^2 (\pi^* 2p_x)^1$

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

N_2^+ and N_2^- have same bond order.

(*d*) He_2^+ has less energy than two isolated He atoms.

C12.(*b,c*) : $O_2^{2-} : (\sigma 1s)^2(\sigma^* 1s)^2(\sigma 2s)^2(\sigma^* 2s)^2(\sigma 2p_z)^2(\pi 2p_x)^2 (\pi 2p_y)^2(\pi^* 2p_x)^2(\pi^* 2p_y)^2$

It is diamagnetic

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

D. mcq based on comprehension

D1. (*c*) : Promotion is not essential condition prior to hybridisation.

D2. (*c*) : NO_2^+ ion is linear. XeF_2 is also linear.

D3. (*b*) : For minimum repulsion, the lone pairs should be present on equatorial positions.

D4. (*c*) : PF_5, ClF_3, SF_4 and XeF_2 involve sp^3d hybridisation. XeF_4 involves sp^3d^2 hybridisation.

D5. (*d*) : XeF_2 has three lone pairs of electrons while all other have one lone pair of electrons.

D7. (*c*) : NO has single electron in π-antibonding MO.

D8. (*b*) : $\sigma 2p_z$ has highest energy.

D9. (*d*) : O_2^{2-} has smallest bond order (1) and therefore, has longest bond length.

D10.(*c*) : F_2 has maximum number of electrons in anti-bonding MOs.

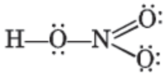
Matching Type Questions

2. (*a*) : (P) XX' – (*iii*) Linear
(Q) XX_3' – (*i*) T-shape
(R) XX_5' – (*iv*) Square pyramidal
(S) XX_7' – (*ii*) Pentagonal bipyramidal

Matrix Match Type Questions

(A) If loss of electron increases bond order, oxidation will be feasible whereas if gain of electron increases bond order, reduction will be feasible. From B_2 to N_2, there is mixing of *s* and *p*-orbitals.

Integer Type Questions

- **1** (4) : O_2^+ CN, NO and N_2^+ have bond order of 2.5.
- **2** (8) : $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2 (\pi 2p_x)^2 (\pi 2p_y)^2 (\pi^* 2p_x)^1$
- **3** (4) : $CuSO_4 . 5H_2O$ has 4 coordinate bonds.
- **4** (2) : B_2 : KK $(\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x)^1 (\pi 2p_y)^1$
- **5** (4) : XeF_4, ClF_3, XeF_2, H_2O
- **6** (5) : H_2O, NF_3, H_2S, CH_3Cl, HI
- **7** (6) : BeH_2, LiCl, BF_3, IF_7, SO_2, PCl_5, H_2SO_4
- **9** (0) : It has distorted geometry because of the presence of lone pair. Therefore, none of the bond angle is of 90°.
- **10** (7) :  No. of lone pairs = 7.
- **11** (0) : There is no F–B–F bond angle of 90°
- **12** (4) : XeF_4, BrF_4^-, $[Cu(NH_3)_4]^{2+}$, $[PtCl_4]^{2-}$ have square planar shape.

  XeF_4 : Square planar, SF_4 : see saw; SiF_4 : tetrahedral, BF_4^- : tetrahedral, BrF_4^- : Square planar; $[Cu(NH_3)_4]^{2+}$: Square planar, $[FeCl_4]^{2-}$: tetrahedral; $[CoCl_4]^{2-}$: tetrahedral $\{PtCl_4]^{2-}$: square planar.
- **13** (4) : The linear molecules and their hybridisation are:

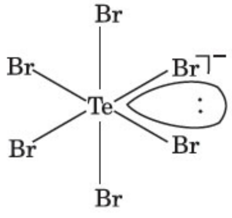
  $BeCl_2$ (*sp*), N_3^- (*sp*), N_2O (*sp*), NO_2^+ (*sp*)

  ICl_2^- (sp^3d), I_3^- (sp^3d), XeF_2 (sp^3d)

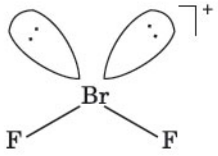
  Thus, there are four linear molecules/ions where the hybridisation of central atom does not have the contribution from the *d*-orbitals.
- **14** (6) : Diamagnetic species are : H_2, Li_2, Be_2, C_2, N_2, F_2.

Competition File

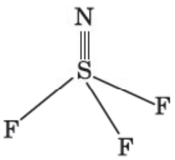
- **15** (6) :



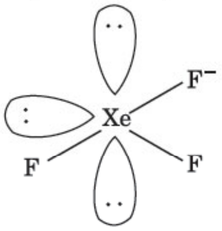
(1 lone pair)



(2 lone pairs)



(no lone pair)

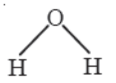


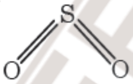
(3 lone pairs)

NCERT Exemplar Problems: MCQ Type-I

1. (*b*) : NF_3 is pyramidal, BF_3 is planar triangular, BF_4^- and NH_4^+ are tetrahedral.
BCl_3 is triangular planer, $BrCl_3$ is pyramidal, NH_3 is pyramidal, NO_3^- is triangular planar.

2. (*c*) : O=C=O H—I

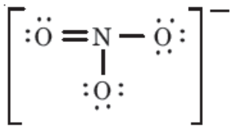




$\mu = 0$ $\mu = 0.38$ D $\mu = 1.84$ D $\mu = 1.62$ D

5. (*c*) : Formal charge on each O atom = $\dfrac{\text{Total charge}}{\text{No. of O atom}}$
$= -3/4 = -0.75$

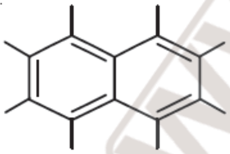
6. (*d*)



Bond pairs = 4, lone pair = 0

7. (*a*) : BH_4^- involves sp^3 hybridisation of B and is tetrahedral.

8. (*c*)



8 C – H, 11 C – C σ bond or 19σ bonds and 5π bonds.

10. (*c*) In C_2H_4, there are two types of bonds C = C and C – H.

11. (*b*) : Only H_2O forms hydrogen bonds.

12. (*d*) : In transition elements, $(n - 1)d$ and ns orbitals take part in bond formation.

14. (*a*) : A represents noble gas Ne.

15. (*b*) : C represent Cl atom. Its stable form is Cl_2 *i.e.*, C_2.

16. (*d*) : B represent P and C represents Cl. The stable compound is PCl_3 *i.e.*, BC_3.

17. (*b*) : Both B and C are non-metals and therefore, bond formed between them will be covalent.

18. (*a*) : The order of energies of MOs for N_2 molecule is:
$\pi 2p_y < \sigma 2p_z < \pi^* 2p_x = \pi^* 2p_y$

19. (*d*) : $\sigma_{2s} < \sigma^*_{2s} < (\pi 2p_x = \pi 2p_y) < \sigma 2p_z < (\pi^* 2p_x = \pi^* 2p_y) < \sigma s^* 2p_z$

20. (*b*) : Bond orders : $O_2 = 2.0$, $O_2{}^+ = 2.5$, $O_2{}^- = 1.5$

$\therefore \quad O_2{}^- < O_2 < O_2{}^+$.

21. (*a*) : The most electronegative element is F having the outermost electronic configuration $2s^2 2p^5$.

NCERT Exemplar Problems: MCQ Type-II

23. (*a*, *b*) Bond orders : $CN^- = 3$, $NO^+ = 3$, $O_2{}^- = 1.5$, $O_2{}^{2-} = 1.0$.

24. (*a*, *d*) Both $BeCl_2$ and S = C = S are linear molecules.

25. (*a*, *b*) Electrons in CO = 6 + 8 = 14, N_2 = 7 + 7 = 14, $SnCl_2$ = 50 + 34 = 84, NO_2^- = 7 + 16 + 1 = 24.

26. (*c*, *d*) Both O_3 and NO_2^- are angular, CO_2 is linear, CCl_4 is tetrahedral.

27. (*c*, *d*) (*a*) The hybridisation is sp^2.
(*b*) In resonance, two C – O bonds and one C = O.
(*c*) Average formal charge on O = $-\dfrac{2}{3} = -0.67$ units.
(*d*) True : all the bond lengths are equal.

28. (*a*, *d*) Bond N_2 and O_2^{2-} are diamagnetic.

29. (*c*, *d*) Bond orders : $N_2 = 3$, $N_2^- = 2.5$, $F_2^+ = 1.5$, $O_2^+ = 1.5$.

NCERT Exemplar Problems: Comprehensive Questions

39 (*a*) : O_2 :

$(\sigma_{1s})^2$	$(\sigma^*_{1s})^2$	$(\sigma_{2s})^2$	$(\sigma^*_{2s})^2$	$(\sigma_{2p_z})^2$
1	2	3	4	5
$(\pi 2p_x)^2$	$(\pi 2p_y)^2$	$(\pi^*_{2p_x})^1$	$(\pi^*_{2p_y})^1$	σ_{2p_z}
6	7	8	9	10

40. (*d*) : Nodal planes are : $\sigma^*_{1s} = 1$, $\sigma^*_{2p_z} = 1$, $\pi_{2p_x} = 1$, $\pi^*_{2p_y} = 2$.

41. (*b*) : O_2^+ and N_2^- have same bond order (2.5). ($O_2 = 2$, $N_2 = 3$, $O_2^+ = 2.5$, $N_2^- = 2.5$, $O_2^+ = 2.5$, $O_2^- = 1.5$)

42. (*c*) : In N_2, $\sigma 2p_z$ MO is filled after $\pi 2p_x$ and $\pi 2p_y$.

Unit Practice Test

for Board Examination

Time Allowed : 1 Hr. ***Maximum Marks : 25***

1. Do N_2^+ and O_2^+ have same bond order. (1)

2. Arrange the following bonds in order of increasing ionic character in the molecules :

$$LiF, K_2O, N_2, SO_2 \text{ and } ClF_3$$ (1)

3. Is there any change in the hybridisation of B and N atoms as a result of the following reaction :

$$BF_3 + NH_3 \longrightarrow F_3B.NH_3$$ (1)

4. Which of the two will have dipole moment ?

cis or trans – C_2H_2Cl (1)

5. How many σ and π bonds are present in naphthalene? (1)

6. Which out of NH_3 and NF_3 has higher dipole moment and why? (2)

7. Do ortho-nitrophenol and para-nitrophenol have hydrogen bonding in their molecules? Explain which of the two has higher boiling point?. (2)

8. Write M.O. electronic configuration of O_2 molecule. Compare its bond order with superoxide ion. (2)

9. Giving one example explain the shapes of following molecules :

(*i*) Molecule containing one lone pair and four bond pairs.

(*ii*) Molecule containing two lone pairs and three bond pairs.

(*iii*) Molecule containing two lone pairs and two bond pairs. (3)

10. Explain the following :

(*i*) Ionic compounds have high melting and boiling points.

(*ii*) Ice floats over water.

(*iii*) BeH_2 molecule has zero dipole moment although the Be—H bonds are polar. (3)

11. Discuss the shapes of following molecules using VSEPR model:

(*i*) $SiCl_4$ (*ii*) PH_3 (*iii*) $BeCl_2$

Which of these is/are polar molecules. (3)

12. (*a*) What is resonance? Write resonance structures of carbon dioxide molecule.

(*b*) Using the concept of hybridisation explain the shapes of

(*i*) C_2H_4 and (*ii*) C_2H_2 molecules.

(*c*) State the type of hybrid orbitals associated with

(*i*) P in PF_5 and (*ii*) S in SF_6 (5)

To check your performance, see HINTS and SOLUTIONS to some questions at the end of Part I of the book.