UNIT 6

Chemical Bonding and Molecular Structure

SYLLABUS

Kossel-Lewis approach to bonding.

Ionic bond—lattice energy, Born-Haber cycle.

Covalent bond—Lewis structure of covalent bond, resonance structures.

Geometry of molecules, VSEPR model, Polarity of bond, Electronegativity, Valence bond approach, concept of resonance, Directional properties of bond.

Hybridization (Qualitative treatment sp, sp^2, sp^3)

6.1. General Introduction— Molecules and Chemical Bond

Atoms are usually not capable of free existence but groups of atoms of the same or different elements exist as one species *e.g.*

H_2, O_2, P_4, S_8, H_2O.

A group of atoms existing together as one species and having characteristic properties is called a molecule.

Obviously, there must be some force which holds these atoms together within the molecules.

This force which holds the atoms together within a molecule is called a chemical bond.

A number of questions now arise :

(*i*) Why do atoms combine ?

(*ii*) Why are only certain combinations possible, *e.g.*, hydrogen exists as H_2 and not as H_3 ?

(*iii*) Why do some atoms combine while certain others do not, *e.g.* two H-atoms combine to form H_2 but two helium atoms do not combine to form He_2 ?

(*iv*) Why do molecules possess definite shapes, *e.g.*, CO_2 is linear but H_2O is tetrahedral ? Similarly, BF_3 is planar but NH_3 is pyramidal.

To look into the reasons for the answers to the above questions, different theories have been put forward from time to time. These are :

1. Kossel-Lewis approach
2. Valence Shell Electron Pair Repulsion (VSEPR) theory
3. Valence Bond Theory
4. Molecular Orbital Theory.

In this unit, the first three theories will be briefly described while molecular orbital theory will be discussed at +2 level.

6.2. Why do Atoms Combine ? Kossel-Lewis Approach

A number of attempts were made to explain the formation of chemical bonds in terms of electrons, but it was only in 1916 when Kossel and Lewis succeded independently in giving a satisfactory explanation. Since their theory was based on the electronic concept of atom, so it is referred to as *Electronic Theory of Valency*. Whereas Kossel's field of study was largely limited to inorganic compounds, Lewis focussed his attention mainly to organic compounds.

The study of noble gases, earlier called inert gases, (Group 18 elements) suggests that neither they combine chemically with any other element nor among themselves. Their electronic configurations are as follows :

Noble gas	*Atomic No.*	*Electronic Configuration*
Helium	2	2
Neon	10	2, 8
Argon	18	2, 8, 8
Krypton	36	2, 8, 18, 8
Xenon	54	2, 8, 18, 18, 8
Radon	86	2, 8, 18, 32, 18, 8

From the study of electronic configurations of the noble gases, it is clear that they are chemically inactive because they have 8 electrons in their outermost orbit except in case of helium which has 2. Hence, it was suggested that they possess stable electronic configurations. In case of all other elements, the number of electrons in their outermost shell is less than 8 and hence they are chemically reactive. This led to the following conclusion :

The atoms of different elements combine with each other in order to complete their respective octets (i.e. 8 electrons in their outermost shell) or duplet (i.e., outermost shell having 2 electrons) in case of H, Li and Be to attain stable nearest noble gas configuration.

6.3. How do Atoms Combine ? (Modes of Chemical Combination)

As discussed above, atoms combine together in order to complete their respective octets so as to acquire the stable inert gas configuration. This can occur in two ways :

1. *By complete transference of one or more electrons from one atom to another*. This process is referred to as **electro-valency** and the chemical bond formed is termed as **electrovalent bond** or **ionic Bond.**

2. *By sharing of electrons.* This can occur in two ways as follows:

(*a*) *When the shared electrons are contributed by the two combining atoms equally, the bond formed is called* **covalent bond.**

(*b*) *When these electrons are contributed entirely by one of the atoms but shared by both, the bond formed is known as* **a co-ordinate bond,** *also called* **dative bond.**

6.4. Lewis Symbols

In the formation of a molecule, only the outer shell electrons are involved and they are known as *valence electrons*. The inner shell electrons are well protected and are generally not involved in the combination process. It is, therefore, quite reasonable to consider the outer shell electrons *i.e.*, valence shell electrons while discussing chemical bonds.

G.N. Lewis introduced simple symbols to denote the valence shell electrons in an atom. The outer shell electrons are shown as dots surrounding the symbol of the atom. These symbols are known as **Lewis symbols** or **electron dot symbols.** These symbols ignore the inner shell electrons. A few examples are given below :

Significance of Lewis symbols. The number of dots around the symbol gives the number of electrons present in the outermost shell. This number of electrons helps to calculate the *common* valency of the elment. That is why these electrons are called *valence shell electrons.*

The common valency of the element is either equal to the number of dots in the Lewis symbol (if these are ≤ 4) or 8 minus the number of dots (if these are > 4)

For example, Li, Be, B and C have valencies 1, 2, 3, and 4 respectively *i.e.* equal to the number of dots whereas valencies of N, O, F and Ne are 3, 2, 1 and 0 respectively *i.e.* 8 minus the number of dots.

Now we shall discuss each type of bond one by one.

6.5. Electrovalent or Ionic Bond

When a bond is formed by complete transference of electrons from one atom to another so as to complete their outermost orbits by acquiring 8 electrons (i.e. octet) or 2 electrons (i.e. duplet) in case of hydrogen, lithium etc. and hence acquire the stable nearest noble gas configuration, the bond formed is called ionic bond or electrovalent bond.

Explanation of the formation of ionic bond. Atoms are electrically neutral. Therefore, they possess equal number of protons and electrons. On losing an electron, an atom becomes positively charged since now the number of protons exceeds the number of electrons.

$$A \longrightarrow A^+ + e^-$$

On the other hand, in case of atom, gaining the electron, the number of electrons exceeds the number of protons and thus the atom becomes negatively charged.

$$B + e^- \longrightarrow B^-$$

The oppositely charged particles formed above attract each other by electrostatic forces of attraction. The bond thus formed is known as *electrovalent or ionic bond.*

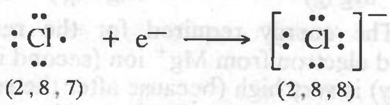
Such a type of bond is formed only when one of the atoms can easily lose electrons while the other can gain electrons and thus each acquires the stable electronic arrangement of the nearest noble gas.

Examples

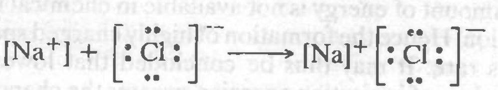
(1) Formation of sodium chloride. Sodium (atomic number = 11) has electronic configuration 2, 8, 1. By losing one electron of its outermost shell, it acquires the inert gas configuration of neon and changes into ion.

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

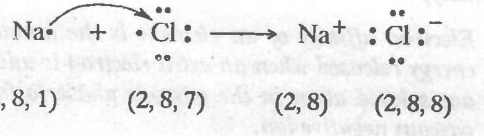
On the other hand, chlorine (atomic number = 17) having electronic configuration 2, 8, 7 accepts one electron released by sodium to complete its octet by attaining stable configuration of argon. In this process, chlorine is converted into chloride ion.



Now we have two species, one is positively charged sodium ion and the other is negatively charged chloride ion. As soon as they approach each other, they are held together by strong electrostatic forces of attraction. Thus, formation of sodium chloride takes place.

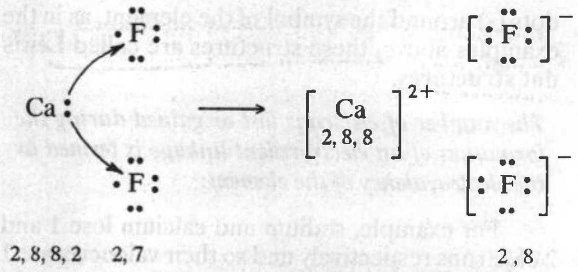


The above steps may be represented directly as follows :



(2) Formation of calcium fluoride. If calcium (atomic No = 20, electronic configuration = 2, 8, 8, 2) loses two electrons, it is converted into calcium ion and attains the stable inert electronic arrangement of argon. On the other hand, fluorine (atomic No. = 9, electronic configuration = 2, 7) on gaining one electron forms fluoride ion and acquires the stable configuration of neon.

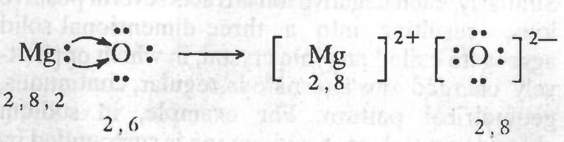
Here, calcium atom loses two electrons and forms calcium ion with two units of postive charge and the two electrons are transferred to two fluorine atoms, which are converted into fluoride ions, each with one unit charge. These oppositely charged ions are then held together by strong electrostatic forces of attraction.



or CaF_2

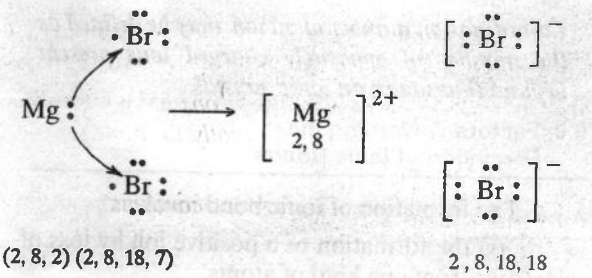
Some More Examples of Formation of Ionic Bonds

(1) Formation of magnesium oxide from magnesium and oxygen.

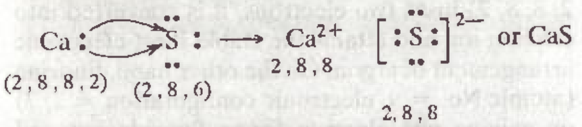


or MgO

(2) Formation of magnesium bromide from magnesium and bromine.

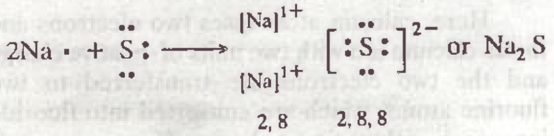


(3) Formation of calcium sulphide.



$$\underset{(2,8,8,2)}{\mathrm{Ca}:}\ \underset{(2,8,6)}{\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{S}}}:} \longrightarrow \underset{2,8,8}{\mathrm{Ca}^{2+}}\ \underset{2,8,8}{\left[:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{S}}}:\right]^{2-}} \text{ or CaS}$$

(4) Formation of sodium sulphide.



$$2\mathrm{Na}\cdot + \overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{S}}}: \longrightarrow \underset{2,8}{\begin{matrix}[\mathrm{Na}]^{1+}\\ [\mathrm{Na}]^{1+}\end{matrix}}\ \underset{2,8,8}{\left[:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{S}}}:\right]^{2-}} \text{ or } \mathrm{Na_2S}$$

When the structures of atoms or ions are written in such a way that the electrons present in the outermost shell (valence shell) are represented by dots (•) around the symbol of the element, as in the examples above, these structures are called **Lewis dot structures.**

The number of electrons lost or gained during the formation of an electrovalent linkage is termed as the electrovalency of the element.

For example, sodium and calcium lose 1 and 2 electrons respectively and so their valencies are 1 and 2. Similarly, chlorine and oxygen gain 1 and 2 electrons respectively, so they possess an electrovalency of 1 and 2. In other words, *valency is equal to the charge on the ion*.

The electrostatic field of an ion is non-directional. Each positive ion attracts several negative ions around it depending upon its size or radius. Similarly, each negative ion attracts several positive ions, resulting into a three dimensional solid aggregate called an ionic crystal, in which oppositvely charged ions alternate in regular, continuous, geometrical pattern. For example, in sodium chloride crystal, each sodium ion is surrounded by six equally spaced chloride ions and each chloride ion by six equally spaced sodium ions, so that there exists an overall electrical neutrality. This is called co-ordination number. Thus co-ordination number of Na^+ and Cl^- ions in NaCl is 6.

Co-ordination number of an ion may be defined as the number of oppositely charged ions present around that ion in an ionic crystal.

6.6. Factors Governing the Formation of Ionic Bonds

The formation of ionic bond involves

(*i*) the formation of a positive ion by loss of electrons from one kind of atoms.

(*ii*) the formation of a negative ion by gain of electrons from another kind of atom.

(*iii*) holding the positive and negative ions by electrostatic forces of attraction.

The formation of ionic bond depends upon the following factors :

(*i*) Ionisation Enthalpy (Ionization Energy).

Ionisation energy of any element is the amount of energy required to remove an electron from the outermost shell of an isolated atom in gaseous phase so as to convert it into a gaseous positive ion.

It is clear that lesser the ionisation energy, easier will be the removal of an electron, *i.e.*, formation of a positive ion and hence greater the chances of formation of an ionic bond. Ionisation energy (I.E.) of alkali metals (*i.e.* group I elements) is low, hence they have more tendency to form positive ions. In case of alkaline earths (*i.e.* group 2 elements), although the formation of positive ions takes place (because ionisation energy is not high) but the I.E.'s are higher than those of group I elements, hence the formation of positive ions is not as easy as in case of alkali metals. For example, in case of sodium, the I.E. is 495 kJ/mole while in case of magnesium, it is 743 kJ/mole. So the formation of positive ion of sodium is easier than that of magnesium.

$$\mathrm{Na}\,(g) \xrightarrow{495\ \mathrm{kJ\ mol^{-1}}} \mathrm{Na}^+\,(g) + e^-$$

$$\mathrm{Mg}\,(g) \xrightarrow{743\ \mathrm{kJ\ mol^{-1}}} \mathrm{Mg}^+\,(g) + e^-$$

The energy required for the removal of second electron from Mg^+ ion (second ionization energy) is very high (because after the removal of the first electron, the effective nuclear charge increases). Hence, the formation of divalent Mg^{2+} ion becomes difficult. Similarly, in case of aluminium, the formation of triply charged Al^{3+} ion requires 3158 kJ/mol^{-1} (as the sum of its 1st, 2nd and 3rd ionisation energies). Thus, it is not generally possible to form this ion since such a huge amount of energy is not available in chemical reaction. Hence the formation of highly charged species is rare. It may thus be concluded that lower the values of ionisation energies, greater the chances of ionic bond formation.

(*ii*) Electron Gain Enthalpy (Electron Affinity)

Electron affinity of an element is the amount of energy released when an extra electron is added to an isolated atom in the gaseous phase to form a gaseous negative ion.

Higher is the electron affinity, more is the energy released and stabler will be the negative ion produced. Consequently, the probability of formation of ionic bond will be enhanced. Halogens possess high electron affinity. So the formation of their negative ions is very common, *e.g.*, in case of chlorine, electron affinity is +348 kJ/mole *i.e.*,

$$Cl\,(g) + e^- \longrightarrow Cl^- + 348\text{ kJ/mole}$$

$$\text{or}\quad E.A. = +348\text{ kJ mol}^{-1}$$

Hence, the halogens can form negative ions easily. On the other hand, elements of group 16 form divalent negative ions (by gaining two electrons) but not so easily. This is because the second electron affinity in case of these elements is much less and is negative *i.e.*, energy is required to form divalent ions. Let us discuss the case of oxygen. First, oxygen will add up one electron to form monovalent ion which is accompanied by release of certain amount of energy. But in the process of addition of second electron to the monovalent oxygen ion, energy is required to overcome the force of repulsion exerted by the negatively charged monovalent ion to the incoming electron.

$$O\,(g) + e^- \longrightarrow O^-\,(g),\qquad EA_1 = +142\text{ kJ mol}^{-1}$$

$$O^-\,(g) + e^- \longrightarrow O^{2-}\,(g),\qquad EA_2 = -693\text{ kJ mol}^{-1}$$

So electron affinity for the overall process will be given by

$$EA = +142 - 693 = -551\text{ kJ mol}^{-1}.$$

The negative sign indicates that energy is required to form divalent oxide ion. Similarly, in case of formation of trivalent negative ions, the amount of energy required will be much higher. Hence, monovalent species are most common, divalent are rare and trivalent are rarer.

Note Carefully that the term used in the above discussion is Electron Affinity (A_e). However, sometimes the term Electron Gain Enthalpy (ΔH_{eg}) is used in place of Electron Affinity (as discussed in unit 4). The two are taken as equal in magnitude (as ΔH_{eg} is only slightly higher than A_e) but opposite in sign. ΔH_{eg} has same sign as required according to thermodynamics *i.e.* if energy is released, it is give a –ve sign. A_e has signs contrary to thermodynamic conventions.

It may be concluded from the above discussion that ionic bonds are generally formed between the atoms of the elements placed on the left and on the right sides of the periodic table.

***(iii)* Lattice Enthalpy (Lattice Energy).** In the formation of ionic compounds, the positively charged ions combine with negatively charged ions to form the compound.

$$A^+ + B^- \longrightarrow A^+B^-$$

The energy released when the requisite number of positive and negative ions combine to form one mole of the ionic compound is called lattice energy.

The higher the value of lattice energy of the resulting ionic compound, the greater will be the stability of the compound and hence greater will be the ease of its formation.

We know that the force of attraction between the oppositely charged ions is directly proportional to the magnitude of the charges (q_1, q_2) and inversely proportional to the square of the distance (d) between them, *i.e.*,

$$\text{Force of attraction} \propto \frac{q_1 \times q_2}{d^2}$$

Hence the value of lattice energy depends upon the following two factors :

***(a)* Charge on the ions.** The higher the charge on the ions, greater is the force of attraction and hence larger is the amount of energy released.

***(b)* Size of the ions.** As highly charged species are rare, the other factor *i.e.*, the internuclear distance between the ions becomes more important. If the size of the ions is large, internuclear distance will be more and force of attraction will be less while in case of small ions, internuclear distance is less and so force of attraction is greater.

Net effect. If Lattice energy + Electron affinity > Ionization energy, the net effect will be the release of energy and hence an ionic bond is formed.

Most of the ionic compounds are formed between cations from metals (because of low ionization energy) and anions from non-metals (because of high electron affinity). However, a very common exception is ammonium ion (NH_4^+) *i.e.* a cation made from two non-metallic elements. A large number of ionic compounds are known in which NH_4^+ is the cation.

6.7. Born-Haber Cycle (Calculation of Lattice Energy—Predicting Stability of a Compound)

Max Born and Fritz Haber in 1919 put forward a method based on Hess's law for the calculation of lattice energy (which could not be measured directly) and hence for predicting the stability of the ionic compound formed (because larger is the negative value for lattice energy, greater is the stability of the compound formed). The method is known as Born-Haber cycle. It is briefly described below taking the example of NaCl (*s*).

The heat of formation of NaCl (*s*) is found to be -411 kJ mol^{-1} *i.e.*

$$Na\,(s) + \tfrac{1}{2}\,Cl_2\,(g) \longrightarrow NaCl\,(s),$$

$$\Delta H^\circ_f = -\,411 \text{ kJ mol}^{-1}$$

We can *imagine* that one mole of NaCl (*s*) can be prepared by the following series of steps :

(*i*) Crystalline sodium metal is sublimed to form gaseous atoms

$$Na\,(s) \longrightarrow Na\,(g),$$

$$\Delta H = \Delta H_{\text{Sublimation}} = S$$

(*ii*) One-half mole of gaseous Cl_2 molecules is dissociated to form 1 mole of gaseous atoms

$$\frac{1}{2}\,Cl_2\,(g) \longrightarrow Cl\,(g),$$

$$\Delta H = \frac{1}{2}\,\Delta H_{\text{disso.}} = \frac{1}{2}D$$

(*iii*) The gaseous Na atoms are ionized to form gaseous sodium ions

$$Na\,(g) \longrightarrow Na^+\,(g) + e^-,$$

$$\Delta H = \text{I.E. (Ionization energy)}$$

(*iv*) The gaseous chlorine atoms are converted into gaseous chloride ions by adding electrons

$$Cl\,(g) + e^- \longrightarrow Cl^-\,(g),$$

$$\Delta H = \text{E.A. (Electron Affinity)}$$

(*v*) The gaseous Na^+ and Cl^- ions combine to form 1 mole of crystalline sodium chloride

$$Na^+\,(g) + Cl^-\,(g) \longrightarrow NaCl\,(s),$$

$$\Delta H = \text{U (Lattice Energy)}$$

The complete process involving the formation of one mole of NaCl (*s*) directly and through a series of steps indirectly may be represented by a cyclic process as under :

$$\begin{tikzcd}
Na\,(s) \arrow[d, "+S"'] & +\ \frac{1}{2}\,Cl_2\,(g) \arrow[d, "+\frac{1}{2}D"'] \arrow[r, "\Delta H^\circ_f"] & NaCl\,(s) \\
Na\,(g) \arrow[d, "+I.E."'] & Cl\,(g) \arrow[d, "-E.A."'] & \\
Na^+\,(g) & Cl^-\,(g) \arrow[uur, "-U"'] &
\end{tikzcd}$$

Applying Hess's law (according to which the heat change is same whether one mole of the compound is formed directly or indirectly through a number of steps), and using the symbols *without proper signs,* we have

$$\Delta H^\circ_f = S + \frac{1}{2}D + I.E. + E.A. + U$$

Substituting the values *with proper signs* (positive sign if energy is absorbed and negative sign if energy is relased), we get for the case of NaCl

$$-411 = +109 + \frac{1}{2} \times 244 + 496 - 349 + U$$

or $U = -789$ kJ

Thus lattice energy for NaCl (*s*) has a large negative value. This explains why the compound NaCl (*s*) is highly stable.

It may be pointed out that direct determination of electron affinity is also very difficult. Accurate values have been obtained only for a few elements. Hence Born-Haber cycle is used for the calculation of electron affinity also using the calculated values of lattice energy from crystal parameters.

Some Important Consequences of Lattice Enthalpies

(*i*) Greater the lattice enthalpy, more stable is the ionic compound.

(*ii*) Greater the lattice enthalpy of an ionic compound, less is its solubility in water.

PROBLEMS ON CALCULATION OF LATTICE ENERGY/ENTHALPY

EXAMPLE. *Calculate the lattice enthalpy of $MgBr_2$. Given that*

Enthalpy of formation of $MgBr_2$ = $-$ 524 kJ mol^{-1}

Sublimation energy of Mg = + 148 kJ mol^{-1}

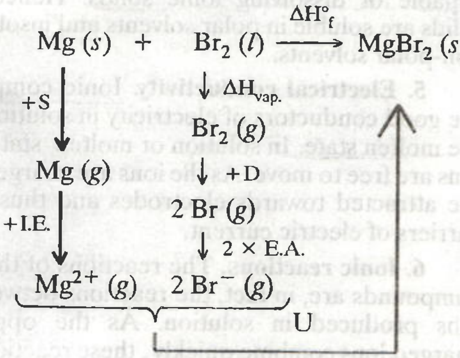
Ionization energy of Mg = + 2187 kJ mol^{-1}

Vaporisation energy of Br_2 (l) = + 31 kJ mol^{-1}

Dissociation energy of Br_2 (g) = + 193 kJ mol^{-1}

Electron gain enthalpy of Br = $-$ 331 kJ mol^{-1}

Solution. Born-Haber cycle for the formation of one mole of $MgBr_2$ may be represented as follows :



$$\Delta H^\circ_f = S + \text{I.E.} + \Delta H_{vap} + D + 2 \times \text{E.A.} + U$$

$$\text{or } U = \Delta H^\circ_f - (S + \text{I.E.} + \Delta H_{vap} + D + 2 \times \text{E.A.})$$

$$= -524 - (148 + 2187 + 31 + 193 - 2 \times 331)$$

$$= -524 - 1897$$

$$= \mathbf{-2421\ kJ\ mol^{-1}}$$

PROBLEMS FOR PRACTICE

1. Calculate the lattice enthalpy of KCl. Given that ΔH_{Sub} of K = + 89 kJ mol^{-1}, $\Delta H_{Diss.}$ for 1 mole of Cl_2 = + 244 kJ mol^{-1}, $\Delta H_{ionization}$ for K (g) = + 425 kJ mol^{-1}, $\Delta H_{electron\ gain}$ for Cl (g) = —355 kJ mol^{-1}, ΔH°_f (KCl) = —438 kJ mol^{-1}.

[Ans. —719 kJ mol^{-1}]

2. Calculate the lattice enthalpy of LiF, given that the enthalpy of (*i*) sublimation of Li is 155·2 kJ mol^{-1} (*ii*) dissociation of half mole of F_2 is 75·3 kJ (*iii*) ionization of Li is 520 kJ mol^{-1} (*iv*) electron gain of 1 mol of F (*g*) is —333 kJ mol^{-1} and (*v*) ΔH°_f for LiF (*s*) is —594·1 kJ mol^{-1}. (*N.C.E.R.T.*)

[Ans. —1011·6 kJ mol^{-1}]

3. Calculate the lattice enthalpy of $CaCl_2$, given that the enthalpy of (*i*) sublimation of Ca is 121 kJ mol^{-1} (*ii*) dissociation of Cl_2 to Cl is 242·8 kJ mol^{-1} (*iii*) ionization of Ca to Ca^{2+} is 2422 kJ mol^{-1} (*iv*) electron gain for Cl to Cl^- is —355 kJ mol^{-1} and (*v*) ΔH°_f for $CaCl_2$ (*s*) is —795 kJ mol^{-1}.

(*N.C.E.R.T.*) **[Ans. —2870·8 kJ mol^{-1}]**

HINTS FOR DIFFICULT PROBLEMS

1. $\Delta H^\circ_f = S + \frac{1}{2} D + \text{I.E.} + \text{E.A.} + U$

$$-438 = 89 + \frac{1}{2}(244) + 425 - 355 + U$$

or $\quad U = -719 \text{ kJ mol}^{-1}$

2. $U = \Delta H^\circ_f - \left[S + \frac{1}{2} D + \text{I.E.} + \text{E.A.}\right]$

$$= -594 \cdot 1 - (155 \cdot 2 + 75 \cdot 3 + 520 - 333)$$

$$= -1011 \cdot 6 \text{ kJ mol}^{-1}$$

3. $U = -795 - [121 + 242 \cdot 8 + 2422 - 2 \times 355]$

$$= -2870 \cdot 8 \text{ kJ mol}^{-1}$$

6.8. General Characteristics of Ionic Compounds

The ionic compounds possess the following characteristics :

1. Physical State. These compounds usually exist in the solid state.

2. Crystal Structure. X-ray analysis of the ionic compounds shows that they exist as ions and not as molecules. These ions are arranged in a regular pattern to form a lattice.

The pattern of arrangement, however, depends upon the size and charges of the ions. For example, in case of sodium chloride, each sodium ion is surrounded by six chloride ions and each chloride by six sodium ions, thus giving rise to a three dimensional octahedral crystal strucutre. The formula of an ionic compound merely indicates the relative number of ions present.

3. High melting and boiling points. Ionic compounds possess high melting and boiling points. This is because ions are tightly held together by strong electrostatic forces of attraction and hence a huge amount of energy is required to break the crystal lattice.

4. Solubility. Electrovalent compounds are soluble in solvents like water which are polar in nature and have high dielectric constant. It is due to the reason that the polar solvent interacts with the ions of the crystals and further the high dielectric constant of the solvent cuts off the force of attraction between these ions. Furthermore, the ions may combine with the solvent to liberate energy called the *hydration energy* which is sufficient to overcome the attractive forces between the ions.

Non-polar solvents like carbon tetrachloride, benzene etc. having low dielectric constants are not capable of dissolving ionic solids. Hence ionic solids are soluble in polar solvents and insoluble in non-polar solvents.

5. Electrical conductivity. Ionic compounds are good conductors of electricity in solution or in the molten state. In solution or molten state, their ions are free to move. As the ions are charged, they are attracted towards electrodes and thus act as carriers of electric current.

6. Ionic reactions. The reactions of the ionic compounds are, in fact, the reactions between the ions produced in solution. As the oppositely charged ions combine quickly, these reactions are, therefore, quite fast.

[*e.g.* $Na^+Cl^- (aq) + Ag^+NO_3^- (aq) \longrightarrow AgCl (s) + NaNO_3 (aq)$].

ADD TO YOUR KNOWLEDGE

1. The concept of ionic bond was put forward by Kossel.
2. The dielectric constant of D_2O is greater than that of H_2O.
3. **Variable electrovalency.** In case of transistion metals, certain atoms can lose different numbr of electrons to acquire a stable configuration. Hence they show **variable electrovalency.** For example, Fe forms Fe^{2+} and Fe^{3+} ions and Cu forms Cu^+ and Cu^{2+} ions. The more stable ion is the one which has more stable core *i.e.* the configuration obtained after the loss of valence electrons. For example, Fe^{3+} salts are more stable than Fe^{2+} salts

$$_{26}Fe = 2, 8, 14, 2$$

$$Fe^{2+} = 2, 8, 14 = [Ne]^{10}\, 3s^2\, 3p^6\, 3d^6 \text{ (unstable core)}$$

$$Fe^{3+} = 2, 8, 13 = [Ne]^{10}\, 3s^2\, 3p^6\, 3d^5 \text{ (stable core)}$$

Cu^{2+} salts are more stable than Cu^+ salts.

$$_{29}Cu = 2, 8, 18, 1$$

$$Cu^+ = 2, 8, 18 = [Ne]^{10}\, 3s^2\, 3p^6\, 3d^{10} \text{ (stable core)}$$

$$Cu^{2+} = 2, 8, 17 = [Ne]^{10}\, 3s^2\, 3p^6\, 3d^9 \text{ (more stable core)}$$

Greater stability of Cu^{2+} than Cu^+ is due to the fact that the nuclear charge of Cu is not sufficient enough to hold 18 electrons of Cu^+ ion present in the outermost shell.

Similarly, in case of heavier *p*-block elements like Sn and Pb with the valence shell configuration $ns^2\, np^2$, all the four electrons may be lost giving a valency of +4 or only *p*-electrons may be lost giving a valency of +2 The *s*-electrons remain attracted by the nucleus due to poor screening effect of the intervening *d* and *f* electrons and do not take part in bonding. The effect is called **inert pair effect.**

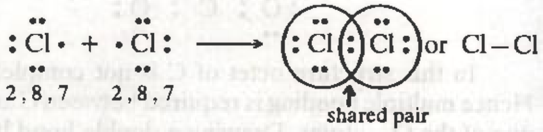
4. For the formation of ionic bond between two atoms, the electronegativity difference between them should be $\geq 1 \cdot 9$.

6.9. Covalent Bond—Lewis-Langmuir Concept

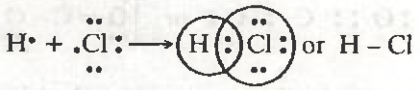
Langmuir, in 1919 improved the Lewis concept by suggesting that when both the atoms taking part in a chemical combination are short of electrons than the nearest noble gas configuration, they can share their electrons in order to complete their octets. Each atom contributes the same number of electrons to form common pairs which are then shared by both atoms.

The bond formed between the two atoms by mutual sharing of electrons between them so as to complete their octets or duplets in case of elements having only one shell is called covalent bond or covalent linkage and the number of electrons contributed by each atom is known as covalency.

Example to illustrate the formation of covalent bond. Let us examine the formation of chlorine molecule. In this case, two chlorine atoms combine to produce chlorine molecule. Each chlorine atom is short of one electron to attain stable configuration of argon. Each of them contributes one electron to form a common shared pair. By doing so, both of them complete their orbits and acquire argon structure. The completed octets are generally represents by enclosing the dots around the symbol by a circle or elipse. Thus



Similarly, in the formation of HCl, H and Cl contribute one electron each which is then shared by both so as to complete duplet of hydrogen and octet of chlorine

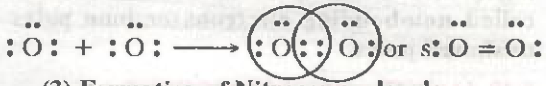


Multiple covalent bonds. In the examples cited above, each atom contributes one electron. Hence the covalency of chlorine and hydrogen is 1. The bond formed is called **single covalent bond** and is represented by single line (–) between the two atoms. Covalent bond may also be formed by the contribution of two or three electrons by each of two atoms. The bond then formed is called **double or triple bond** and are represented by a double line (=) and a triple line (≡) respectively.

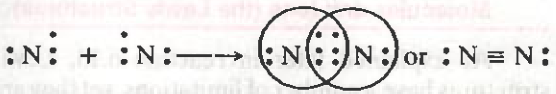
Some More Examples of Formation of Covalent Bonds

(1) Formation of Hydrogen molecule

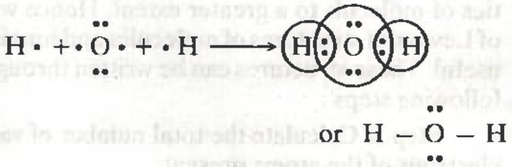
(2) Formation of Oxygen molecule



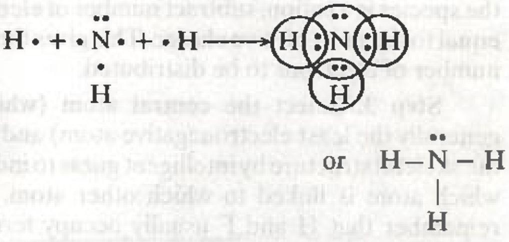
(3) Formation of Nitrogen molecule



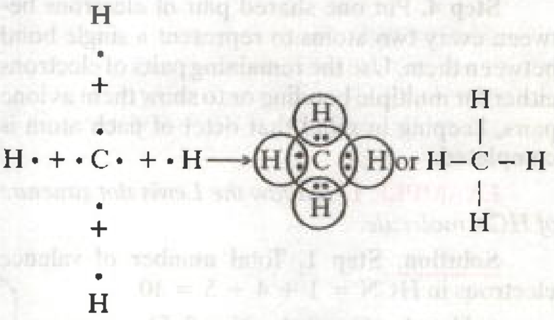
(4) Formation of H_2O molecule



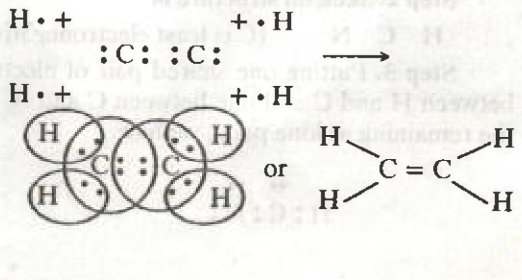
(5) Formation of NH_3 molecule



(6) Formation of Methane (CH_4) molecule



(7) Formation of Ethylene (C_2H_4) molecule



Bond Pairs and Lone Pairs. The shared pairs of electrons present between the atoms are called **bond paris** because they are responsible for the bonding between the atoms. On the other hand, the valence electrons not involved in bonding (*i.e.*, sharing) are shown as such and are called **non-bonding electrons** *or* **lone pairs** *or* **unshared pairs.**

6.10. Lewis Representation of Simple Molecules and Ions (the Lewis Structures)

As explained later in reaction 6.13, Lewis structures have a number of limitations, yet they are helpful in understanding the formation and properties of moleculs to a greater extent. Hence writing of Lewis dot structures of molecules and ions is very useful. These structures can be written through the following steps :

Step 1. Calculate the total number of valence electrons of the atoms present.

Step 2. If the species is an anion, add number of electrons equal to the units of – ve charge and if the species is a cation, subtract number of electrons equal to the units of + ve charge. This gives the total number of electrons to be distributed.

Step 3. Select the central atom (which is generally the least electronegative atom) and draw the skeletal structure by intelligent guess to indicate which atom is linked to which other atom. Also remember that H and F usually occupy terminal position.

Step 4. Put one shared pair of electrons between every two atoms to represent a single bond between them. Use the remaining pairs of electrons either for multiple bonding or to show them as lone pairs, keeping in mind that octet of each atom is completed.

EXAMPLE 1. *To draw the Lewis dot structure of HCN molecule.*

Solution. Step 1. Total number of valence electrons in HCN = 1 + 4 + 5 = 10

$({}_1H = 1,\ {}_6C = 2, 4,\ {}_7N = 2, 5)$

Step 2. Skeletal structure is

H C N (C is least electronegative).

Step 3. Putting one shared pair of electrons between H and C and one between C and N, and the remaining as lone pairs, we have

$$H:\ddot{C}:\ddot{N}:$$

In this structure, duplet of H is complete but octets of C and N are not complete. Hence multiple bonding is required between C and N. Octets of C and N will be complete if there is triple bond between C and N. Thus we have

$$H:C\vdots\vdots\ddot{N} \quad \text{or} \quad H-C\equiv\ddot{N}$$

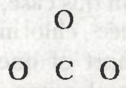
EXAMPLE 2. *To draw the Lewis dot structure of CO_3^{2-} ion.*

Solution. Step 1. Total number of valence electrons of $CO_3 = 4 + 3 \times 6 = 22$

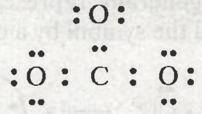
$({}_6C = 2, 4,\ {}_8O = 2, 6)$

Step 2. Total number of electrons to be distributed in $CO_3^{2-} = 22 + 2 = 24$

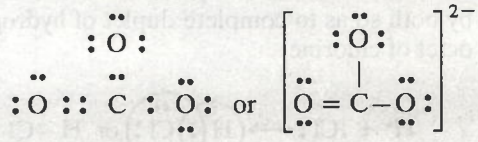
Step 3. The skeletal structure of CO_3 is



Step 4. Putting one shared pair of electrons between each C and O and completing the octets of oxygen, we have



In this structure octet of C is not complete. Hence multiple bonding is required between C and one of the O – atoms. Drawing a double bond between C and one O-atom serves the purpose



Alternatively, the structure may be obtained through the following steps :

Step 1. Calculate the total number of valence electrons (A) after subtracting for the cation or adding for the anion.

Step 2. Calculate the number of electrons (N) for complete octets of all the atoms.

Step 3. Calculate shared pair of electrons (S) by subtracting A from N *i.e.* S = N – A.

Step 4. Draw the skeletal structure and represent the shared pairs.

Step 5. Complete the structure by representing the unshared electrons (U = A – S).

EXAMPLES. (*i*) *To draw Lewis structure of CO_2*

Step 1. A = 1 × 4 (for C) + 2 × 6 (for O)
= 4 + 12 = 16 electrons.

Step 2. N = 1 × 8 (for C) + 2 × 8 (for O)
= 8 + 16 = 24 electrons.

Step 3. S = N – A = 24 – 16 = 8 electrons (shared).

Step 4. Drawing skeletal structure with shared pairs

$$O::C::O$$

Step 5. U = A – S = 16 – 8 = 8.

∴ Complete Lewis structure will be

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

(*ii*) *To draw the Lewis structure of CN^- ion*

Step 1. A = 1 × 4 (for C) + 1 × 5 (for N) + 1 (for negative charge) = 10 electrons.

Step 2. N = 1 × 8 (for C) + 1 × 8 (for N)
= 16 electrons.

Step 3. S = N – A = 16 – 10 = 6 electrons (shared).

Step 4. Drawing skeletalstructure with shared pairs

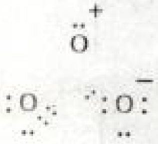
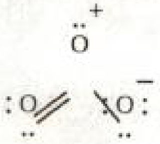
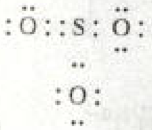
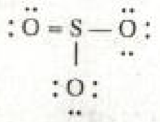
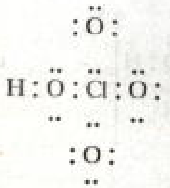
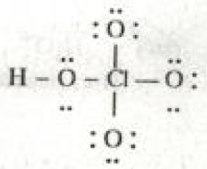
$$C\vdots\vdots N^-$$

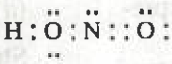
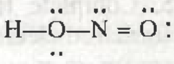
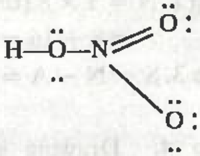
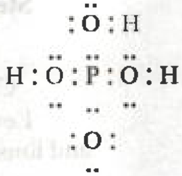
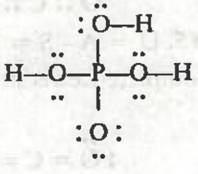
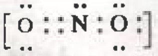
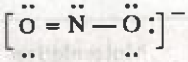
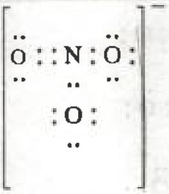
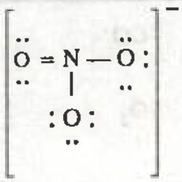
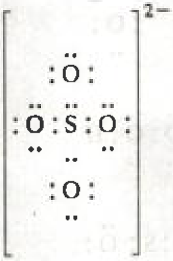
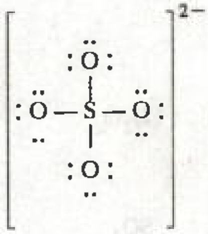
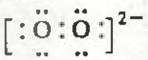
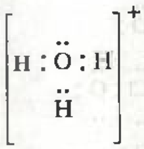
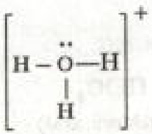
Step 5. U = A – S = 10 – 6 = 4

∴ Complete Lewis structure will be $\overline{:C\vdots\vdots N:}$

Lewis structures of some typical molecules and ions are given in the Table 6.1 below :

TABLE 6.1. Lewis structures of some typical molecules and ions

Molecule/Ion		Lewis Representation		
(*i*)	CO	$:C::\overset{..}{}O:$	or	$:C\equiv O:$
(*ii*)	O_2	$:\ddot{O}::\ddot{O}:$	or	$:\ddot{O}=\ddot{O}:$
(*iii*)	O_3		or	
(*iv*)	H_2O_2	$H:\underset{..}{\ddot{O}}:\underset{..}{\ddot{O}}:H$	or	$H-\underset{..}{\ddot{O}}-\underset{..}{\ddot{O}}-H$
(*v*)	SO_3	 $:\ddot{O}::\underset{\underset{..}{:O:}}{S}:\underset{..}{\ddot{O}}:$	or	 $:\ddot{O}=\underset{\underset{..}{:O:}}{\underset{\vert}{S}}-\underset{..}{\ddot{O}}:$
(*vi*)	$HClO_4$ (Perchloric acid)	 $H:\underset{..}{\ddot{O}}:\overset{:\ddot{O}:}{\underset{\underset{..}{:O:}}{\underset{..}{\ddot{Cl}}}}:\underset{..}{\ddot{O}}:$	or	 $H-\underset{..}{\ddot{O}}-\overset{:\ddot{O}:}{\underset{\underset{..}{:O:}}{\underset{\vert}{Cl}}}-\underset{..}{\ddot{O}}:$

(*vii*) HNO_2 (Nitrous acid)	 or 
(*viii*) HNO_3 (Nitric acid)	 or 
(*ix*) H_3PO_4 (Phosphoric acid)	 or 
(*x*) NO_2^- (Nitrite ion)	 or 
(*xi*) NO_3^- (Nitrate ion)	 or 
(*xii*) SO_4^{2-} (Sulphate ion)	 or 
(*xiii*) O_2^{2-} (Peroxide ion)	 or 
(*xiv*) H_3O^+ (Hydronium ion)	 or 

6.11. Formal Charge (F.C.) on an atom in a molecule/ion

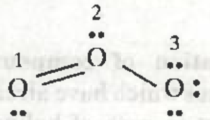
In a molecule, there is no charge on the molecule as a whole or in a polyatomic ion (*e.g.* CO_3^{2-} or NH_4^+ ion etc.) although the charge present on the ion is the charge on the ion as a whole and not on the individual atoms, yet for some purposes, it is useful to assign a formal charge to each atom in a molecule or ion.

The formal charge on an atom in a molecule or ion is defined as the difference between the number of valence electrons of that atom in the free state and the number of electrons assigned to that atom in the Lewis structure, assuming that in each shared pair of electrons, the atom has one electron of its own and the lone pair on it belongs to it completely. Thus it can be calculated as follows :

$$\left[\begin{array}{c}\text{Formal charge (F.C.) on}\\ \text{an atom in a molecule/ion}\end{array}\right] = \left[\begin{array}{c}\text{Total no. of valence electrons}\\ \text{in the free atom}\end{array}\right] - \left[\begin{array}{c}\text{Total no. of electrons of}\\ \text{lone pairs (non-bonding electrons)}\end{array}\right] - \frac{1}{2}\left[\begin{array}{c}\text{Total no. of shared electrons}\\ \text{(bonding electrons)}\end{array}\right]$$

EXAMPLE 1. *Calculate formal charge on each O-atom of O_3 molecule.*

Solution. Lewis structure of O_3 is as follows :



The atoms have been numbered as 1, 2 and 3.

Formal charge on end O-atom numbered 1

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

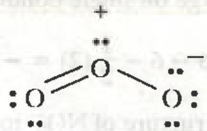
Formal charge on central O-atom numbered 2

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

Formal charge on end O-atom numbered 3

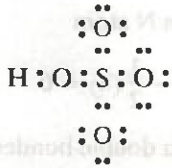
$$= 6 - 6 - \frac{1}{2}(2) = -1$$

Hence we represent O_3 alongwith formal charges as follows :



EXAMPLE 2. *Calculate the formal charge on (i) S in HSO_4^- ion (ii) Cl in $HClO_4$*

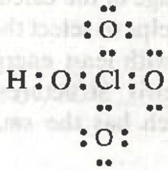
Solution. (*i*) Lewis structure of HSO_4^- ion is



Applying the formula for calculation of formal charge.

Formal charge on $S = 6 - 0 - \frac{1}{2}(8)$
$= 6 - 4 = +2$

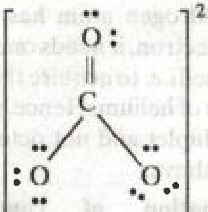
(*ii*) Lewis structure of $HClO_4$ is



Formal charge on $Cl = 7 - 0 - \frac{1}{2}(8) = +3$

EXAMPLE 3. *Write the formal charges on atoms in (i) carbonate ion (ii) nitrite ion* (N.C.E.R.T.)

Solution. (*i*) Lewis structure of CO_3^{2-} ion is



Formal charge on C atom

$$= 4 - 0 - \frac{1}{2}(8) = 0$$

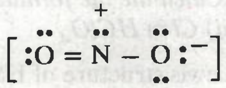
Formal charge on double bonded O atom

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

Formal charge on single bonded O atom

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

(*ii*) Lewis structure of NO_2^- ion is



$$\left[:\ddot{O} = \overset{+}{\ddot{N}} - \ddot{\underset{..}{O}}:^-\right]$$

Formal charge on N atom

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

Formal charge on double bonded O atom

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

Formal charge on single bonded O atom

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

The main advantage of the calculation of formal charges is that it helps to select the most stable structure *i.e.* the one with least energy out of the different possible Lewis Structures. The most stable is the one which has the smallest formal charges on the atoms.

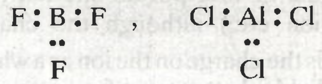
6.12. Exceptions to Octet Rule

Although octet rule is able to explain the formation of a large number of compounds, there are some exceptions to this rule as follows :

(*i*) **Formation of compounds involving hydrogen.** As hydrogen atom has only one shell containing one electron, it needs one more electron to complete its shell *i.e.* to acquire the nearest noble gas configuration of helium. Hence hydrogen needs to complete its duplet and not octet, as explained in the examples above.

(*ii*) **Formation of compounds like $BeCl_2$, BF_3, $AlCl_3$ etc.** In each of these molecules, the central atom (Be, B or Al) has less than 8 electrons *i.e.* these are electron deficient compounds as shown below :

$:\ddot{\underset{..}{Cl}}:Be:\ddot{\underset{..}{Cl}}:$ (Be has 4 electrons around it)

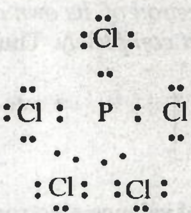


$$F:\underset{\underset{F}{..}}{B}:F\;,\qquad Cl:\underset{\underset{Cl}{..}}{Al}:Cl$$

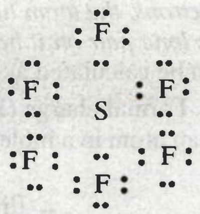
(B and Al have 6 electrons around them)

Thus octet rule is violated.

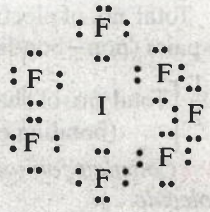
(*iii*) **Formation of compounds like PCl_5, SF_6, IF_7 etc.** In each of these molecules, the central atom has more than 8 electrons (expanded octects) as shown below :



(10 e⁻ around P)



(12 e⁻ around S)

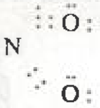
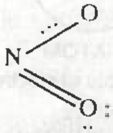


(14 e⁻ around I)

Again the octet rule is violated in these molecules.

(*iv*) **Formation of compounds of noble gases.** Noble gases which have already completed octets (or duplet in case of helium) should not form compounds. However, their compounds like XeF_2, XeF_4, XeF_6, KrF_2 etc. have been actually prepared.

(*v*) **Odd electron bonds/Odd electron molecules.** There are some molecules and ions in which the bonded atoms contain odd number of electrons (usually 3) between them. The bonds thus present are called odd electron bonds and the molecules are called odd electron molecules. Some common examples are given below :

Molecule/Ion	Lewis Representation		
(*i*) Nitric oxide (NO)		or	
(*ii*) Nitrogen dioxide (NO_2)		or	
(*iii*) Oxygen molecule (O_2)		or	
(*iv*) Superoxide ion (O_2^-)		or	

A three electron bond is considered to be equivalent to half covalent bond.

6.13. Limitations of Lewis—Langmuir Concept of Covalent Bond

Lewis – Langmuir concept of covalent bond, as explained in sec. 6.9, has the following limitations :

(*i*) It could not explain how the atoms are held together in the molecules like H_2, Cl_2 etc. in which there are no ions and hence there are no electrostatic forces of attraction *i.e.* it could not explain the formation of a covalent bond.

(*ii*) It could not explain the shapes of molecules containing covalent bonds.

(*iii*) It could not explain the release of energy during the formation of a covalent bond.

To explain the above limitations, two important theories called **modern theories** of covalent bond formation have been put forward. These are based on *quantum mechanical principles*. These are :

(1) Valence Bond (VB) theory

(2) Molecular Orbital (MO) theory

In the next section, we shall take up a brief discussion of Valence Bond theory only and that too in a simple manner without entering into the mathematical complexity involved. The discussion of Molecular Orbital theory will be taken up at + 2 level.

6.14. Valence Bond Theory of Covalent Bond (Orbital Concept)

This theory was put forward by Heitler and London in 1927 and further developed by Pauling and others. According to this approach,

A covalent bond is formed by the partial overlap of two half-filled atomic orbitals containing electrons with opposite spins.

The 'partial overlap' means that a part of the electron cloud of each of the two half-filled atomic orbitals becomes common. As a result, the probability of finding the electrons in the region of overlap is much more than at other places. Thus, the two electrons (with opposite spins) although keep on exchanging position between the two atoms but are present for maximum time in the region of overlap and hence are attracted to both the nuclei simultaneously thereby forming a bond between the two atoms.

The strength of the bond depends upon the extent of overlapping. Greater the overlapping, stronger is the bond formed.

To understand the concept more clearly, let us consider the following examples :

(i) Formation of Hydrogen Molecule : When two hydrogen atoms having electrons with opposite spins come close to each other, their s-orbitals overlap with each other resulting in the union of two atoms to form a molecule (Fig. 6.1).

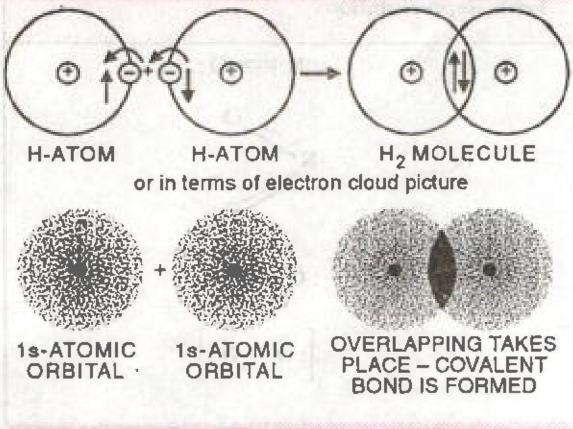


FIGURE 6.1. Formation of hydrogen molecule.

(ii) Formation of Hydrogen Fluoride Molecule : In case of formation of hydrogen fluoride molecule, when one atom of fluorine (elecronic configuration : $1s^2\,2s^2\,2p_x^2\,2p_y^2\,2p_z^1$) having one unpaired electron in its *p*-orbital comes closer to hydrogen atom with electron of opposite spin in its 1*s*-orbital, then the two half-filled orbitals overlap each other and a chemical bond is formed between the two atoms. This is shown in Fig. 6.2.

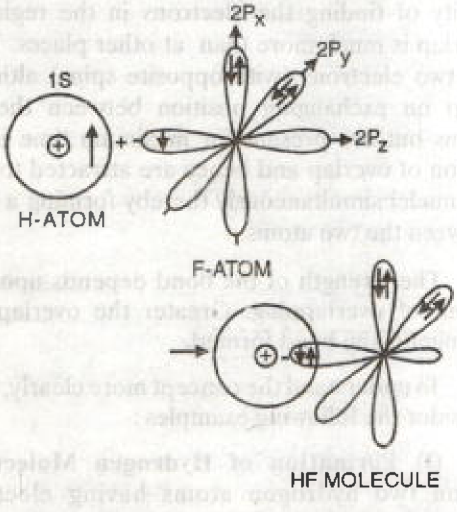


FIGURE 6.2. Formation of HF molecule.

(iii) Formation of Fluorine Molecule : When an atom of fluorine (electronic configuration : $1s^2\,2s^2\,2p_x^2\,2p_y^2\,2p_z^1$) approaches another atom of fluorine having an electron of opposite spin in $2p_z$ orbital, the half-filled orbitals overlap each other resulting in the formation of a fluorine molecule as shown in Fig. 6.3.

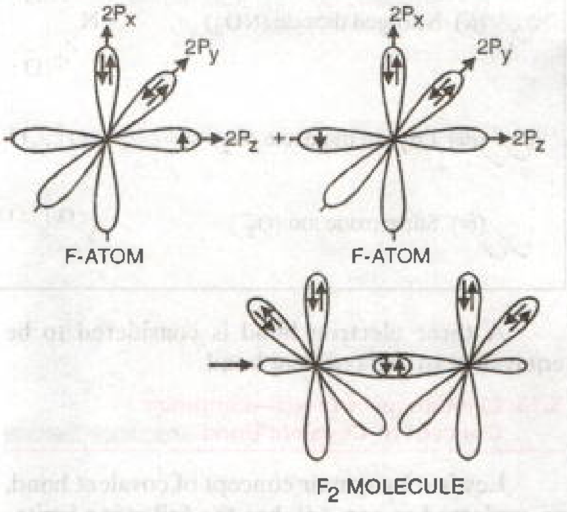


FIGURE 6.3. Formation of Fluorine Molecule.

Difference in the strengths of bonds in H_2, HF and F_2. As the orbitals involved in the overlap are different, the extent of overlap is different and hence the strength is different.

Existence of only H_2 and non-existence of species like H_3, H_4 etc. This can be easily explained on the basis of orbital concept. A hydrogen atom contains only one half-filled atomic orbital (1*s*) which can overlap with the half-filled atomic orbital of another hydrogen atom only, forming H_2. No more half- filled atomic orbital is available and so no more bond can be formed.

Non-formation of He_2. This can also be explained on the basis of orbital concept. A helium atom contains fully-filled atomic orbital ($1s^2$) which cannot overlap with the 1*s* orbital of another helium atom because only half-filled atomic orbitals can overlap with each other. Thus He_2 is not formed.

Interpretation of orbital overlap in terms of energy consideration. Taking the example of the formation of H_2 molecule, when the two atoms are far apart from each other, there is no interaction between them. When they come closer to each other, the new forces come into operation. These forces are of two types :

---

*Their bond strengths are in the order $F-F < H-H < H-F$.

(*i*) *The forces of repulsion between the nuclei of these combining atoms and between the electrons of these atoms*. These forces tend to increase the energy of the system.

(*ii*) *The forces of attraction between the nucleus of one atom and electrons of the other atom.* These forces tend to decrease the energy of the system.

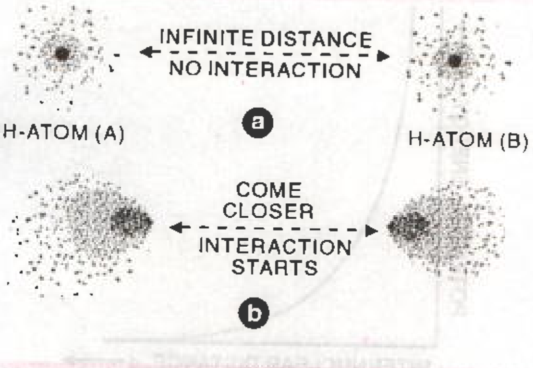


FIGURE 6.4. (a) No interactions at large distances (b) Interactions start as atoms come closer.

If in a system, these new forces can decrease the energy, then possibility of chemical bonding exists and if these forces lead to increase in energy, the chemical bonding is not possible. For more clarification, let us disucss formation of hydrogen molecule.

Suppose we have two hydrogen atoms A and B kept at infinite distance from each other. There will be no interaction between them. But as they begin to come closer, the following new forces will start operating :

(*i*) Force of attraction between nucleus of A and electrons of B.

(*ii*) Force of attraction between nucleus of B and electrons of A.

(*iii*) Force of repulsion between electrons of the atoms.

(*iv*) Force of repulsion between nuclei of the two atoms.

The diagrammatic representation of these forces is given in Fig. 6.5.

In case of hydrogen, the magnitude of the attractive forces is more than that of the repulsive forces. As a result, the potential energy of the system decreases and a molecule of hydrogen is formed. The energy changes taking place during the formation of hydrogen molecule are shown graphically in Fig. 6.6.

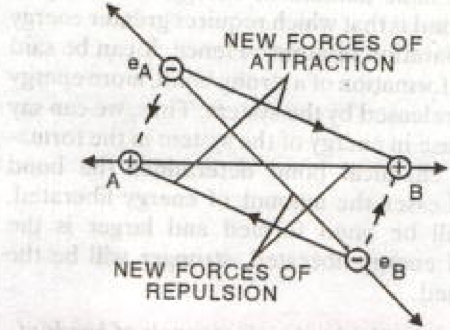


FIGURE 6.5. New forces of attraction and repulsion between two H-atoms approaching each other.

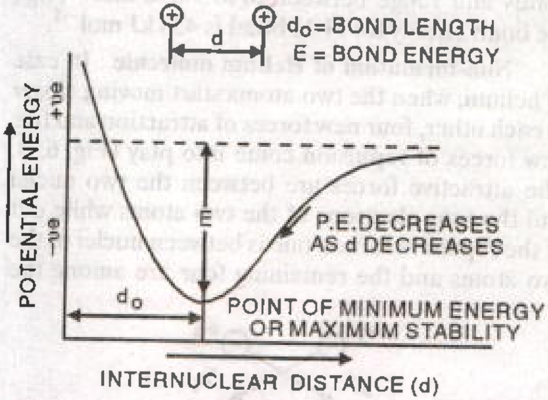


FIGURE 6.6. Potential energy diagram showing variation of energy with internuclear distance between two H-atoms.

As the atoms start coming closer to each other from infinite distance, they start interacting with each other and the system starts losing its energy as the forces of attraction exceed the forces of repulsion. But at a certain equilibrium distance, the forces of repulsion are just balanced by the forces of attraction and the energy of the system becomes minimum. In this situation, the two hydrogen atoms are said to be bonded together to form a stable system *i.e.*, a molecule.

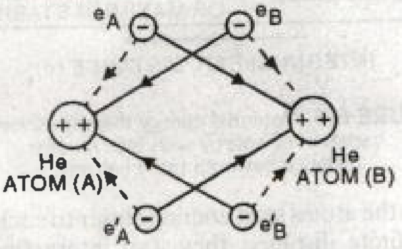
At this stage, the distance between the two nuclei is called bond length and in case of hydrogen, it is 74 pm. If we try to bring these atoms still closer, then repulsive forces start overpowering the attractive forces. Consequently, energy of the system increases causing instability to the system.

In the formation of a chemical bond, a certain amount of energy is released. If we want to break the bond, *i.e.*, to separate the atoms, we have to supply the same amount of energy. Obviously a stronger bond is that which requires greater energy for the separation of atoms. Hence, it can be said that in the formation of a strong bond, more energy should be released by the system. Thus, we can say that decrease in energy of the system in the formation of a chemical bond determines the bond strength. Lesser the amount of energy liberated, weaker will be bond formed and larger is the amount of energy liberated, stronger will be the bond formed.

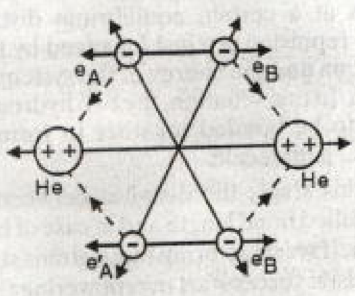
The energy required to break one mole of bonds of the same kind is known as bond energy or bond dissociation energy.

The bond energies are different for differnet bonds and range between 20 to 540 kJ mol^{-1}, *e.g.*, the bond energy for H-H bond is 436 kJ mol^{-1}.

Non-formation of Helium molecule : In case of helium, when the two atoms start moving closer to each other, four new forces of attraction and five new forces of repulsion come into play (Fig. 6.7). The attractive forces are between the two nuclei and the four electrons of the two atoms while out of the repulsive forces, one is between nuclei of the two atoms and the remaining four are among the electrons. As a result of these new interactions, repulsive forces overpower the attractive forces and so the energy of the system increases. Hence, no chemical bond is possible.



NEW FORCES OF ATTRACTION SHOWN BY SOLID LINES



NEW FORCES OF REPULSION SHOWN BY SOLID LINES

FIGURE 6.7. New forces of attraction and repulsion in case of the helium atoms approaching each other.

Thus energetically the formation of helium molecule is not possible because there is an increase in the potential energy of the systen when two helium atoms approach each other (Fig. 6.8).

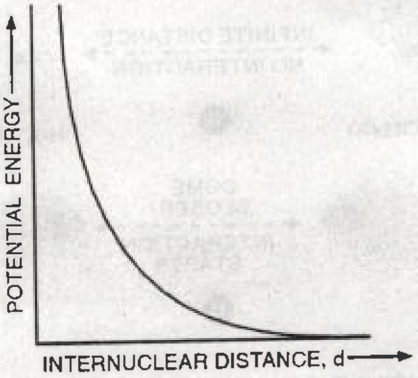


FIGURE 6.8. Variation of potential energy when two helium atoms are brought closer.

6.15. Types of Covalent Bonds— Sigma and PI Bonds

Depending upon the type of overlapping, the covalent bonds are mainly of two types :

1. Sigma (σ) bond

When a bond is formed between two atoms by the overlap of their atomic orbitals along the internuclear axis (end to end or head on overlap), the bond formed is called sigma (σ) bond.

The overlapping along the internuclear axis can take place in any one of the following ways :

(i) s-s overlapping : This type of overlapping takes place between atoms having half-filled *s*-orbitals in their outermost energy shell. For example, in the formation of hydrogen molecule, 1*s* orbital of one hydrogen atom overlaps with 1*s* orbital of other hydrogen atom thus forming a sigma bond (Fig. 6.9). Similarly, in case of lithium hydride, 1*s*-orbital of hydrogen overlaps with 2*s*-orbital of lithium.

(ii) s-p overlapping : In this case, half-filled *s*-orbital of one atom overlaps with the half-filled *p*-orbital of another atom. A simple example of this type is the formation of hydrogen fluoride. Here, 1*s* orbital of hydrogen overlaps with $2p_z$ orbital of fluorine (Fig. 6.10).

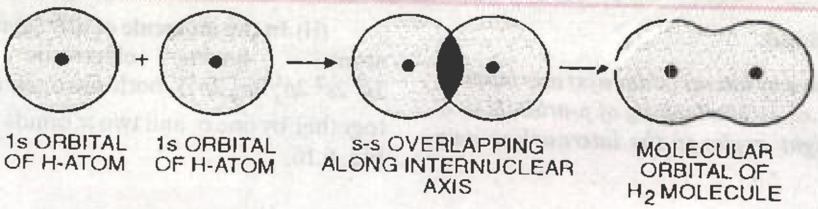


FIGURE 6.9. Formation of H_2 molecule (s-s overlapping).

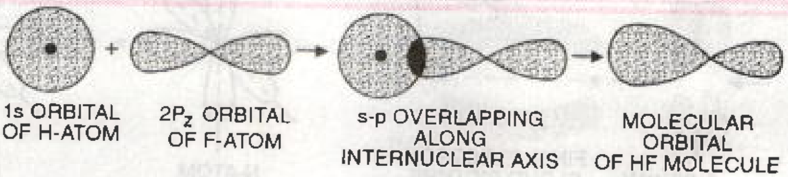


FIGURE 6.10. Formation of HF molecule (s-p overlapping).

(iii) p-p overlapping : This type of overlapping occurs when *p*-orbital of one atom overlaps with the *p*-orbital of the other as in case of fluorine molecule. The electronic configuration of fluorine is $1s^2\,2s^2\,2p_x^2\,2p_y^2\,2p_z^1$ (*i.e.* it has a half-filled $2p_z$ orbital). The molecule of fluorine is produced by the overlapping of $2p_z$ orbitals of the two fluorine atoms as shown in the Fig. 6.11.

FIGURE 6.11. Formation of F_2 molecule (p-p overlapping).

Similarly, the formation of Cl – Cl and Br – Br can be explained.

Summing up, a sigma bond is formed by overlapping of (*i*) s-s orbitals (*ii*) s-p orbitals (*iii*) p-p orbitals along the internuclear axis as represented in Fig. 6.12.

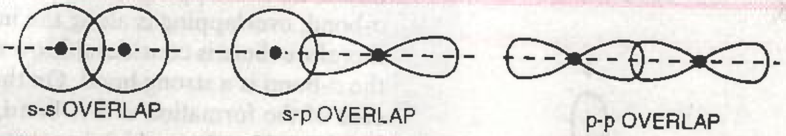


FIGURE 6.12. Representation of s-s, s-p and p-p overlapping forming σ bonds.

Note. If Z-axis is chosen as the internuclear axis, no overlapping can take place between *s* and p_x or p_y orbital or p_x and p_y orbitals *i.e.* there is zero overlap (Fig. 6.13).

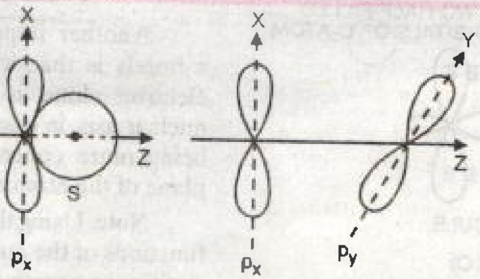


FIGURE 6.13. No overlapping is possible between p_x and s orbitals and between p_x and p_y orbitals

2. Pi (π) Bond.

Pi-bond is formed by lateral (sideways) overlapping of p-orbitals, i.e., by overlapping of p-orbitals in a direction at right angles to the internuclear axis (Fig. 6.14).

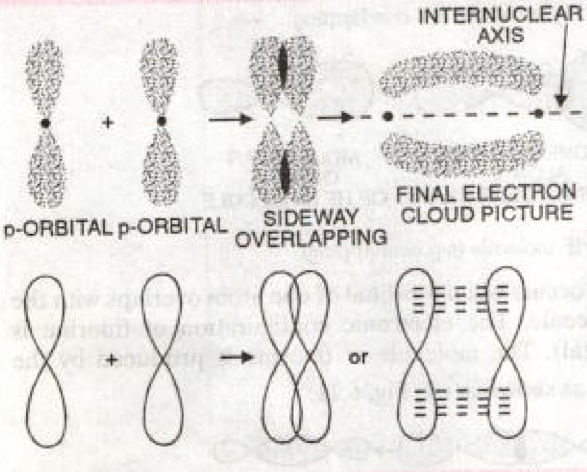


FIGURE 6.14. p-p overlapping forming a pi bond.

A π-bond is seldom formed between atoms unless accompanied by a σ-bond. For example,

(i) In case of oxygen molecule (each oxygen atom having electronic configuration, $1s^2\ 2s^2\ 2p_x^2\ 2p_y^1\ 2p_z^1$), the two atoms are held together by one σ- bond and one π-bond as shown in Fig. 6.15.

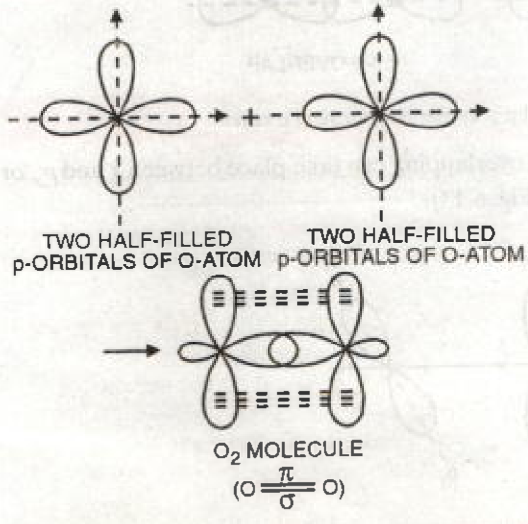


FIGURE 6.15. Formation of oxygen molecule.

(ii) In the molecule of nitrogen (each nitrogen atom having electronic configuration, $1s^2\ 2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^1$), both nitrogen atoms are held together by one σ and two π bonds as shown in the Fig. 6.16.

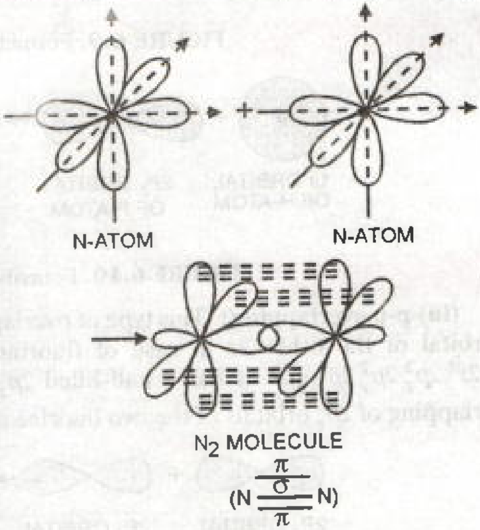


FIGURE 6.16. Formation of nitrogen molecule.

(iii) In case of ethylene, double bond between two carbon atoms consists of one sigma bond and one π bond (as discussed later in section 6.25).

The strength of a bond depends upon the extent of overlapping. Since in the formation of σ-bond, overlapping is along the internuclear axis, therefore there is considerable overlapping. Hence the σ-bond is a strong bond. On the other hand, in case of the formation of a π-bond, sideways overlapping takes place which is only to a small extent. Hence, π-bond is a weak bond.

For the same reason, the strength of the three types of σ-bonds is in the order

$$s-s > s-p > p-p$$

Another important aspect about the σ and π-bonds is that whereas in case of σ-bond, the electron cloud is symmetrical about the internuclear axis, in case of π-bond, it is unsymmetrical, being more concentrated above and below the plane of the atomic nuclei.

Note. Using the appropriate signs for the wave functions of the atomic orbitals, the overlap can be positive or negative or zero as shown in Fig. 6.17 on the next page.

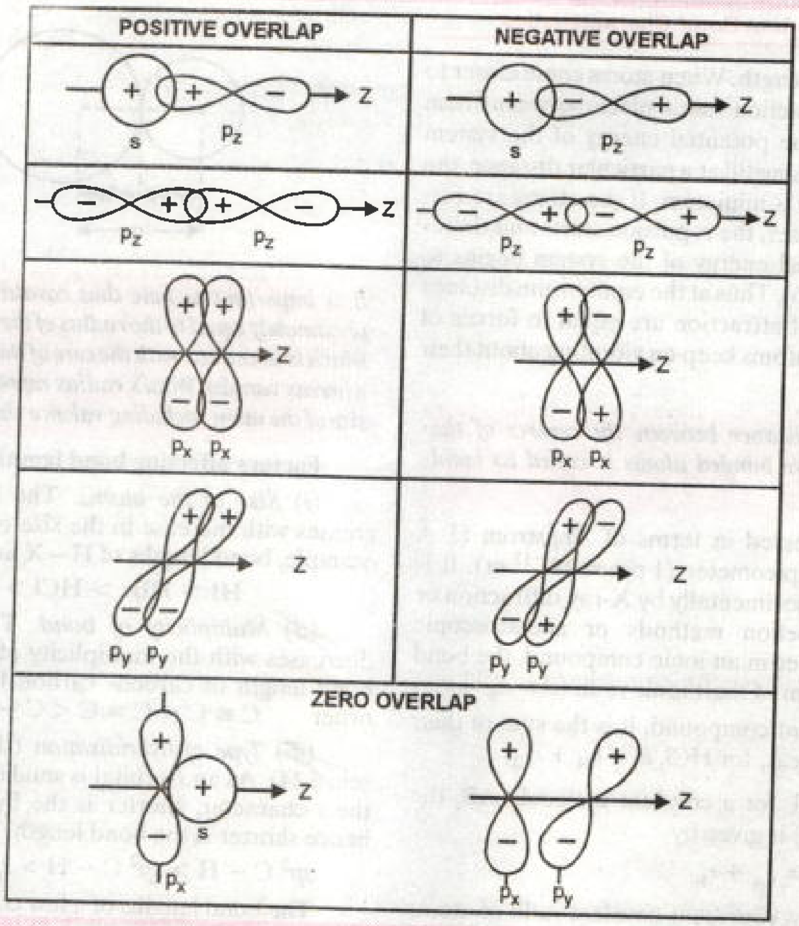


FIGURE 6.17. Depiction of positive, negative and zero overlap.

Comparison of Sigma and Pi Bonds. Some important points of difference between sigma and *pi* bond are listed in Table 6.2.

TABLE 6.2. Comparison of sigma and pi bonds

SIGMA (σ) BOND	Pi (π) BOND
(*i*) This bond is formed by overlap of orbitals along their internuclear axis (end to end overlap).	(*i*) This is formed by sideway overlapping of orbitals (lateral overlapping).
(*ii*) This is formed by overlapping between s-s, s-p or p-p orbitals.	(*ii*) This is formed by the overlap of p-p orbitals only.
(*iii*) Overlapping is quite large and hence sigma bond is a strong bond.	(*iii*) Overlapping is to a small extent. Hence π-bond is a weak bond.
(*iv*) Electron cloud in this case is symmetrical about the line joining the two nuclei.	(*iv*) Electron cloud of π-bond is unsymmetrical.
(*v*) Sigma bond consists of only one electron cloud, symmetrical about the internuclear axis.	(*v*) Pi (π) bond consists of two electron clouds, one above the plane of atomic nuclei and the other below it.
(*vi*) Free rotation about a σ-bond is possible.	(*vi*) Free rotation about a π-bond is not possible because on rotation, overlapping vanishes and so the bond breaks.

6.16. Some Important Bond Characteristics

(1) Bond Length. When atoms come closer to each other, attraction takes place between them and therefore the potential energy of the system keeps on decreasing till at a particular distance, the potential energy is minimum. If the atoms are further brought closer, the repulsion starts and therefore the potential energy of the system begins to increase (Fig. 6.6). Thus at the equilibrium distance (where forces of attraction are equal to forces of repulsion), the atoms keep on vibrating about their mean positions.

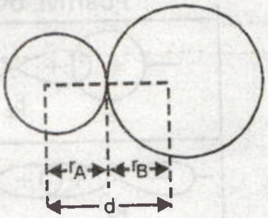
The average distance between the centres of the nuclei of the two bonded atoms is called its bond length

It is expressed in terms of Angstrom (1 Å $= 10^{-10}\ m$) or picometer (1 pm $= 10^{-12}\ m$). It is determined experimentally by X-ray diffraction or electron diffraction methods or spectroscopic methods. Further in an ionic compound, the bond length is the sum of their ionic radii ($d = r_+ + r_-$) and in a covalent compound, it is the sum of their covalent radii (*e.g.*, for HCl, $d = r_H + r_{Cl}$)

In general, for a covalent molecule AB, the bond length (d) is given by

$$d = r_A + r_B$$

where r_A and r_B represent covalent radii of atoms A and B respectively



It is important to note that covalent radius is approximately equal to the radius of the core of the atom which is in contact with the core of the adjoining atom whereas van der Waal's radius represents the overall size of the atom including valence shell.

Factors affecting bond length

(*i*) *Size of the atoms.* The bond length increases with increase in the size of the atoms. For example, bond lengths of H – X are in the order

HI > HBr > HCl > HF

(*ii*) *Multiplicity of bond.* The bond length decreases with the multiplicity of the bond. Thus bond length of carbon- carbon bonds are in the order $C \equiv C < C = C < C - C$

(*iii*) *Type of hybridisation* (discussed later in sec. 6.24). As an *s*-orbital is smaller in size, greater the *s*-character, shorter is the hybrid orbital and hence shorter is the bond length. For example,

sp^3 C – H > sp^2 C – H > sp C – H

The bond lengths of a few common bonds are given in Table 6.3 below :

TABLE 6.3. Bond length of some common bonds

Bond	Bond length (pm)	Bond	Bond length (pm)
H—H	74	H—Cl	127
Cl—Cl	199	H—Br	141
O = O	120	H—I	161
C—C	154	C—H	109
C = C	134	C—Cl	177
C ≡ C	120	O—H	96

(2) Bond Enthalpy (Bond Energy). When atoms come close together resulting in the formation of bond between them, energy is released. Conversely, the energy is required to break the bond to get the separated atoms.

The amount of energy required to break one mole of bonds of a particular type so as to separate them into gaseous atoms is called bond dissociation energy or simply bond energy.

Bond energy is usually expressed in kJ mol^{-1}. Further, greater is the bond dissociation energy, stronger is the bond.

For diatomic molecules like H_2, Cl_2, O_2, N_2, HCl, HBr, HI etc., the bond energies are equal to their dissociation energies and hence have fixed values. In case of polyatomic molecules, since a particular type of bond present in different molecules (*e.g.,* O – H bond in H – O – H or CH_3O – H etc.) or even in the same molecule (*e.g.,* four C – H bonds in CH_4) do not possess the same bond energy (due to change in chemical environment), therefore bond energies are usually the *average values.*

The bond energies of some common bonds have been given in Table 5.1 of Unit 5.

Factors affecting bond energy

(*i*) *Size of the atoms.* Greater the size of the atoms, greater is the bond length and less is the bond dissociation energy *i.e.* less is the bond strength.

(*ii*) *Multiplicity of bonds.* For the bond between the same two atoms, greater is the multiplicity of the bond, greater is the bond dissociation energy. This is firstly because atoms come closer and secondly, the number of bonds to be broken is more.

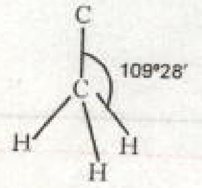
(*iii*) *Number of lone pairs of electrons present.* Greater the number of lone pairs of electrons present on the bonded atoms, greater is the repulsion between the atoms and hence less is the bond dissociation energy. For example for a few single bonds, we have

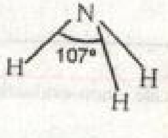
Bond	C—C	N—N	O—O	F—F
Lone pairs of electrons on each atom	0	1	2	3
Bond energy (kJ mol^{-1})	348	163	146	139

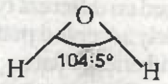
(3) Bond Angle. We know that a bond is formed by the overlap of atomic orbitals. The direction of overlap gives the direction of the bond.

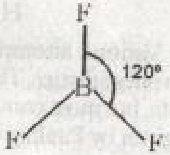
The angle between the lines representing the directions of the bonds i.e. the orbitals containing the bonding electrons is called the bond angle.

It is expressed in degrees, minutes and seconds. For example, H – C – H bond angle in CH_4, H – N – H bond angle in NH_3, H – O – H bond angle in H_2O and F – B – F bond angle in BF_3 are shown below :









(4) Bond Order. *In the Lewis representation of a molecule or ion, the number of bonds present between two atoms is called bond order.* For example, the bond orders of a few molecules are given below :

Molecule :	H – H	O = O	N ≡ N	C ≡ O
Bond order :	1	2	3	3

For odd electron molecules, as the three electron bond is considered as equivalent to half covalent bond, bond order can be fractional also.

For example, Lewis structure of NO is $:\dot{N}=\ddot{O}:$ (See page 6/15). Hence its bond order = $2\frac{1}{2}$.

It is interesting to observe that isoelectronic species have the same bond order *e.g.*

(*i*) F_2 and O_2^{2-} have 18 lectrons each and each of them has a bond order = 1.

(*ii*) N_2, CO and NO^+ have 14 electrons each and each of them has a bond order = 3.

Further, it is also observed that

(*i*) Greater the bond order, greater is the stability of the bond *i.e.* greater is the bond enthalpy.

(*ii*) Greater the bond order, shorter is the bond length.

6.17. Electronegativity

Electronegativity of an element is the tendency of its atom to attract the shared pair of electrons towards itself in a covalent bond. It is represented by χ (pronounced as kii).

It differs from electron affinity, ionisation energy etc. in the sense that these relate to atoms in their isolated states, whereas electronegativity is a property of an atom in the bonded state.

Let us consider two atoms which are not identical, *e.g.,* hydrogen and chlorine forming the covalent compound HCl. Since the electronegativity of chlorine is greater than that of hydrogen, the former attracts shared pair of electrons more than the latter. So chlorine end of the molecule becomes slightly negative and the hydrogen end becomes slightly positive. Thus HCl is a polar molecule which may be represented as :

$$\overset{+\delta}{\mathrm{H}} \text{———} \overset{-\delta}{\mathrm{Cl}}$$

Various attempts have been made to measure electronegativities. These were based on different types of data, but most common and widely accepted pattern was given by Pauling based on bond energy data.

According to **Pauling**, the difference in the electronegativities of two atoms bonded together (A – B) is related to the excess bond energy of A – B than the average value of bond energies of A – A and B – B according to the equation

$$|\chi_A - \chi_B| = 0\cdot102\sqrt{\Delta}$$

where $\Delta = \text{B.E. (A – B)} - \dfrac{\text{B.E. (A – A)} + \text{B.E. (B – B)}}{2}$

and is expressed in **kJ mol^{-1}**.

Thus greater the value of the excess energy, Δ, larger is the difference in the electronegativities of the bonded atoms A and B.

Fluorine is the most electronegative element and earlier it was given a value of 4·0 on the Pauling scale. The relative electronegativities of other atoms are calculated using the above equation and are given in Table 6.4.

Another useful scale of electronegativity has been put forward by **Mulliken.** It is based on the concept that if an atom has high electron affinity (or low electron gain enthalpy) and high ionization energy, it will attract the electrons towards itself and hence will have high electronegativity. If the conditions are opposite, the atom will have a tendency to lose electrons *i.e.* it will have little tendency to attract electrons towards itself and hence will have low electronegativity. Mulliken* electronegativity of an element can be calculated from the ionization energy (I.E.) and electron affinity (E.A.) or electron gain enthalpy (ΔH_{eg}) values according to the equation

$$\chi_M = \frac{1}{2}(\text{I.E.} + \text{E.A.}) = \frac{1}{2}(\text{I.E.} - \Delta H_{eg})$$

(It may be recollected that EA and ΔH_{eg} are taken as equal in magnitude but opposite in sign)

Mulliken's values of electronegativity are given in brackets in the Table 6.4.

It is interesting to note that Mulliken's values become equal to Pauling values if $\frac{1}{2}$(I.E. + E.A.) values in *e*V are divided by 3.17.

TABLE 6.4. Electronegativity values of representative elements

GROUP 1	GROUP 2	GROUP 13	GROUP 14	GROUP 15	GROUP 16	GROUP 17
H 2·20 (3·06)						
Li 0·98 (1·28)	Be 1·57 (1·98)	B 2·04 (1·83)	C 2·55 (2·67)	N 3·04 (3·08)	O 3·44 (3·22)	F 3·92 (4·43)
Na 0·93 (1·21)	Mg 1·31 (1·63)	Al 1·61 (1·37)	Si 1·90 (2·03)	P 2·19 (2·39)	S 2·58 (2·65)	Cl 3·16 (3·54)
K 0·82 (1·03)	Ca 1·00 (1·30)	Ga 1·81 (1·34)	Ge 2·01 (1·95)	As 2·18 (2·26)	Se 2·55 (2·51)	Br 2·96 (3·24)
Rb 0·82 (0·99)	Sr 0·95 (1·21)	In 1·78 (1·30)	Sn 1·96 (1·83)	Sb 2·05 (2·06)	Te 2·10 (2·34)	I 2·66 (2·88)
Cs 0·79	Ba 0·89	Tl 2·04	Pb 2·33	Bi 2·02		

Values without the brackets are on Pauling scale

Values in brackets are on Mulliken's scale.

---

*Mathematical calculation of electronegativity based on Mulliken scale – non-evaluative.

How electronegativity is different from electron affinity ?

(*i*) Electronegativity is the property of the atom only in the *bonded state* as it is the relative tendency of the atom to attract the **shared pair** of electrons towards itself. On the other hand, electron affinity refers to the **gain of electron** by an *isolated atom.*

(*ii*) Electron affinity can be measured experimentally whereas electronegativity is only a relative number with respect to fluorine taken as 4·0.

6.18. Polar and Non-polar Covalent Bonds

1. Non-polar Covalent Bonds. If two similar atoms come close to each other and form a bond by sharing their electrons, the shared electrons are equally attracted by the two atoms as the electronegativity of the atoms is same. In other words, the shared electrons are not displaced towards any one atom. Hence, no poles are developed. This leads to the formation of completely non-polar bond. For example, if two hydrogen atoms form a bond, the electron pair will lie exactly in the middle between the two atoms and the resultant bond is non-polar (Fig. 6.18).

The important characteristic of a non-polar bond is that the electron cloud is completely symmetrical and there is no charge separation at all.

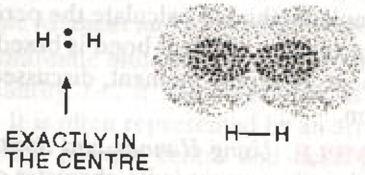


FIGURE 6.18. Non-polar covalent bond between H-atoms.

The examples of some non-polar molecules are Cl_2 , O_2 , N_2 etc.

2. Polar Covalent Bonds. When two dissimilar atoms, having different electronegativities combine together to form a covalent bond, the shared pair of electrons does not lie at equal distances from the nuclei of both the bonded atoms but shifts towards the atom having greater electronegativity. Since the more electronegative atom attracts the electrons more strongly, the distribution of electrons gets distorted, *i.e.*, the electron cloud is displaced more towards the more electronegative atom. As a result, one end of the molecule, having more electronegative atom becomes slightly negatively charged while the other end acquires slightly positive charge. Thus positive and negative poles are developed and this type of bond is called polar covalent bond (or covalent bond with partial ionic character).

Let us consider the case of hydrogen chloride molecule. Chlorine is more electronegative than hydrogen. So the force of attraction, on the shared pair, exerted by chlorine is more than that by hydrogen. Hence it will be shifted towards chlorine, *i.e.*, electron density of the electron cloud is more concentrated on chlorine side than on the hydrogen side. Consequently, chlorine becomes slightly negatively charged and hydrogen becomes slightly positively charged (Fig. 6.19).

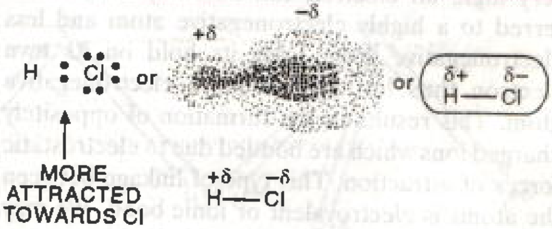


FIGURE 6.19. Polar covalent bond in HCl.

Molecules having polar covalent bond are called polar molecules. Another common example of a polar molecule is that of BrCl or ICl in which Cl is more electronegative than Br or I as shown in Fig. 6.20.

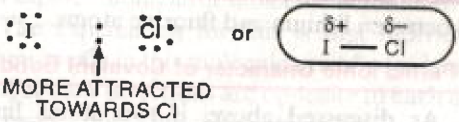


FIGURE 6.20. Polar covalent bond in ICl.

Examples of some other molecules containing more than one polar bond are shown in Fig. 6.21.

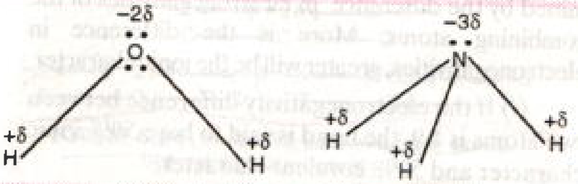


FIGURE 6.21. Polar molecules containing more than one polar pond.

Again, in case of symmetrical molecules like boron trifluoride (BF_3), methane (CH_4) and carbon tetrachloride (CCl_4), the molecular dipole moment is found to be zero. This is again because of the fact that individual dipole moments cancel out on account of the symmetry of the molecule as shown in Fig. 6.25. For example in case of BF_3, the resultant of two bond moments, being equal and opposite to that of the third, cancels out.

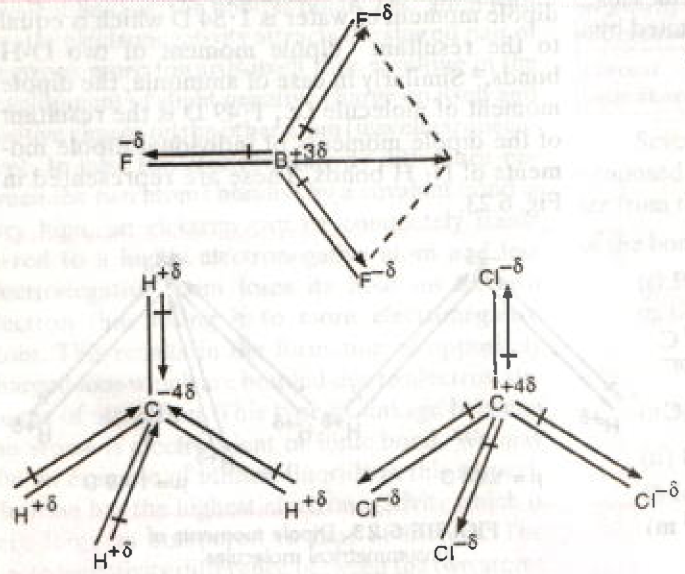


FIGURE 6.25. Dipole moments of zero for symmetrical molecules.

Applications of Dipole Moment :

(1) In determining the polarity of bonds. As $\mu = q \times d$, obviously, greater is the magnitude of dipole moment, higher will be the polarity of the bond. But in the strict sense, this concept is applicable to molecules containing only one polar bond. Further in case of non-polar molecules like H_2, O_2, N_2 etc., the dipole moment is found to be zero. This is because there is no charge separation in these molecules, *i.e.*, $q = 0$. Thus dipole moment can also be used to distinguish between polar and non-polar molecules.

(2) In the calculation of percentage ionic character. This may be illustrated with the following examples :

EXAMPLE 1. *Calculate the percent ionic character of HCl. Given that the observed dipole moment is 1·83 D and bond length of HCl is 1·275 Å.*

Solution. If HCl were 100% ionic, each end would carry charge equal to one unit viz $4{\cdot}8 \times 10^{-10}$ e.s.u. As bond length of HCl is 1·275 Å, its dipole moment for 100% ionic character would be

$$\mu_{ionic} = q \times d$$
$$= 4{\cdot}8 \times 10^{-10}\ \text{e.s.u.} \times 1{\cdot}275 \times 10^{-8}\ \text{cm}$$
$$= 6{\cdot}12 \times 10^{-18}\ \text{e.s.u. cm}$$
$$= 6{\cdot}12\ \text{D}$$
$$\mu_{observed} = 1{\cdot}03\ \text{D (Given)}$$
$$\therefore\ \%\ \text{ionic character} = \frac{\mu_{observed}}{\mu_{ionic}} \times 100$$
$$= \frac{1{\cdot}03}{6{\cdot}12} \times 100 = \mathbf{16{\cdot}83\%}$$

EXAMPLE 2. *The dipole moment of LiH is $1{\cdot}964 \times 10^{-29}$ Cm and the interatomic distance between Li and H in the molecule is 1·596 Å. Calculate the percent ionic character of the molecule.*

Solution. If the molecule were 100% ionic,

$$\mu_{\text{ionic}} = q \times d$$
$$= (1{\cdot}602 \times 10^{-19}\ \text{C}) \times (1{\cdot}596 \times 10^{-10}\ m)$$
$$= 2{\cdot}557 \times 10^{-29}\ \text{Cm}$$
$$\mu_{observed} = 1{\cdot}964 \times 10^{-29}\ \text{Cm}\ (Given)$$
$$\therefore\ \%\ \text{ionic character} = \frac{\mu_{observed}}{\mu_{ionic}} \times 100$$
$$= \frac{1{\cdot}964 \times 10^{-29}\ \text{Cm}}{2{\cdot}557 \times 10^{-29}\ \text{Cm}} \times 100$$
$$= 76{\cdot}81\%.$$

PROBLEMS FOR PRACTICE

The observed dipole moment for a molecule AB is 1·45 D and its bond length is 1·654 Å. Calculate the percentage of ionic character in the bond. *(Bihar C.E.C.E. 2000)* [**Ans.** 18·3%]

(3) In determining the symmetry (or shape) of the molecules. Dipole moment is an important factor in determining the shape of molecules containing three or more atoms. For instance, if any molecule possesses two or more polar bonds, it will not be symmetrical if it possesses some molecular dipole moment as in case of water ($\mu = 1 \cdot 84$ D) and ammonia ($\mu = 1 \cdot 49$ D). But if a molecule contains a number of similar atoms linked to the central atom and the overall dipole moment of the molecule is found to be zero, this will imply that the molecule is symmetrical, *e.g.*, in case of BF_3, CH_4, CCl_4 etc.

6.21. Characteristics of Covalent Compounds

1. Physical State. Unlike ionic compounds (which generally exist as solids), the covalent compounds exist in all the three states, viz., solid, liquid and gaseous.

2. Crystal Structure. The crystal structure of covalent compounds differs from that of ionic compounds. They usually consist of molecules rather than ions.

3. Melting and Boiling Points. Covalent compounds have low melting and boiling points because the molecules in covalent compounds are held together less rigidly (by weak van der Waal's forces), than in case of ionic compounds.

4. Solubility. Covalent compounds are generally soluble in organic (non-polar or weakly polar) solvents but insoluble in water and other polar solvents.

5. Electrical conductivity. Since there are no free ions in covalent compounds to conduct electricity, they are bad conductors of electricity.

6. Non-ionic reactions. Since these compounds are molecular in nature and not ionic, their reactions are molecular and proceed at a much slower rate than those of ionic compounds.

7. Directional characteristics and Isomerism. As the atoms in covalent compounds are held together by the shared electrons and not by the electrostatic force, it is rigid and directional. Hence atoms in a molecule can take up different directional arrangements and thus show structural and stereo-isomerism.

6.22. Comparison between the Properties of Elecrtrovalent and Covalent Compounds

The main points of difference between electrovalent and covalent ocmpounds are summed up in Table 6.5.

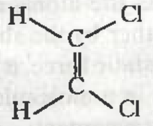
TABLE 6.5. Comparison of electrovalent and covalent compounds

ELECTROVALENT OR IONIC COMPOUNDS	COVALENT COMPOUNDS
(*i*) They are formed by complete transference of electrons from one atom to another. $A\cdot + \cdot\ddot{\underset{\cdot\cdot}{B}}: \longrightarrow A^{+}\left[:\ddot{\underset{\cdot\cdot}{B}}:\right]^{-}$	(*i*) They are formed by sharing of electrons between the two atoms. $:\ddot{\underset{\cdot\cdot}{A}}\cdot + \cdot\ddot{\underset{\cdot\cdot}{B}}: \longrightarrow :\ddot{\underset{\cdot\cdot}{A}}:\ddot{\underset{\cdot\cdot}{B}}:$
(*ii*) These compounds are generally solids.	(*ii*) These compounds may be solids or liquids or gases.
(*iii*) They are made up of ions with powerful electrostatic forces of attraction.	(*iii*) They are made up of molecules held together by weak van der Waal's forces of attraction.
(*iv*) They have generally high melting and boiling points.	(*iv*) They have generally low melting and boiling points.
(*v*) Ionic compounds are generally soluble in polar solvents such as water and insoluble in organic solvents.	(*v*) Covalent compounds are generally soluble in non-polar solvents such as benzene and insoluble in polar solvents such as water.
(*vi*) Ionic compounds conduct electricity in the molten or dissolved state.	(*vi*) Covalent compounds are generally bad conductors of electricity.
(*vii*) Ionic bonds are non-directional and these compounds do not show isomerism.	(*vii*) Covalent bonds are rigid and directional. These compounds show isomerism.
(*viii*) These compounds undergo ionic reactions which are very fast, almost instantaneous.	(*viii*) These compounds undergo molecular reactions which are very slow.

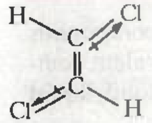
ADD TO YOUR KNOWLEDGE

1. $FeCl_3$ has greater covalent character than $FeCl_2$. This is because Fe^{3+} ion has greater charge and smaller size than Fe^{2+} ion. As a result, Fe^{3+} ion has greater polarizing power (Refer to Fajan's rules discussed on page 6/68, 69).
2. Solubility of aluminium halides is in the order $AlF_3 > AlCl_3 > AlBr_3 > AlI_3$. This is because as the size of the anion increases, it gets more and more easily polarized and hence covalent character of the molecule increases (Refer to Fajan's rules on page 6/68, 69).
3. Dipole moment also helps to determine the following :

   (*i*) *To distinguish between cis and trans isomers.* This is based on the fact that cis isomer usually has higher dipole moment than trans-isomer *e.g.*



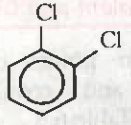
cis ($\mu \neq 0$)



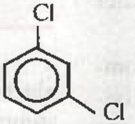
trans ($\mu = 0$)

1, 2-Dichloroethene ($\leftarrow\!\!\!+$ shows direction of dipole moment)

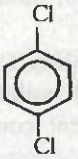
   (*ii*) *To distinguish between ortho, meta and para isomers.* This is based on the fact that the dipole moment of *p*-isomer = 0 and that of ortho is greater than that of meta *e.g.*



ortho–
$\mu = 2{\cdot}54$ D



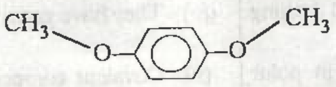
meta–
$\mu = 1{\cdot}48$ D



para–
$\mu = 0$

Dichlorobenzene

4. **Variable and maximum covalency.** As covalency is equal to the number of half-filled orbitals, therefore if the central atom of a molecule has empty *d*-orbitals in the valence shell, the paired electrons from *s* and *p*-orbitals of the valence shell may be unpaired due to excitation to empty *d*- orbitals. As a result, number of half-filled orbitals increases and so is the covalency. For example, ${}_{15}P = [Ne]^{10}\, 3\,s^2\, p_x^1\, 3p_y^1\, 3p_z^1$. Then it shows a covalency of 3 as in PCl_3. In the excited state, we have ${}_{15}P = [Ne]^{10}\, 3\,s^1\, 3p_x^1\, 3\,p_y^1\, 3\,p_z^1\, 3\,d^1$. Thus it will show a covalency of 5 as in PCl_5. Similarly, we have SF_4 and SF_6. *The maximum covalency is equal to the number of electrons present in the s and p-orbitals of the valence shell in the ground state.*
5. For *p*-dimethoxy benzene, $\mu \neq 0$. This is because the structure of this compound is



6. The maximum number of covalent bonds formed between two atoms is never greater than three.
7. A π-bond is never formed alone. It is formed alongwith a σ-bond.
8. H-atom always forms only one σ-bond in the covalent compounds.

6.23. Valence Shell Electron Pair Respulsion Theory

As already explained, Lewis concept is unable to explain the shapes of molecules. The first simple theory that was put forwad to explain the shapes of molecules is known as Valence Shell Electron Pair Repulsion (VSEPR) theory. This theory was given by Sidgwick and Powell in 1940 and was further improved by Nyholm and Gillespie in 1957. The basic concept of this theory is as follows :

The central atom is linked to other atoms by covalent bonds which are formed by sharing of electrons. Thus, the central atom is surrounded by shared pairs (or bond pairs) of electrons and there may be some lone pairs of electrons also present (which have not taken part in the formation of bonds). The stability of the molecule demands that it should have minimum energy. If the electron pairs surrounding the central atom are nearer, they will repel each other, thereby increasing the energy of the molecule. But if the electron pairs are far apart, the repulsions between them will be less and so the energy of the molecule will be low. Thus the main idea of the VSEPR theory is as under :

The electron pairs surrounding the central atom repel one another and move so far apart from one another that there are no further repulsions between them. As a result, the molecule has minimum energy and maximum stability.

Since after repulsions between them, the electron pairs take up definite positions around the central atom, hence the molecule has a definite shape or geometry.

The above concept leads to the following results (called the **basic assumptions** of the VSEPR theory) which help to find the shape of a molecule :

(1) The shape of a molecule containing only two atoms is always linear.

(2) For molecules containing 3 or more atoms, one of the atoms is called the central atom to which other atoms are linked.

(3) If the central atom is linked to similar atoms and is surrounded by bond pairs of electrons only, the repulsions between them are similar. As a result, the shape of the molecule is *symmetrical* and the molecule is said to have a *regular geometry*.

(4) If the central atom is linked to different atoms or is surrounded by bond pairs as well as lone pairs of electrons, the repulsions between them are different*. As a result, the molecule has an *irregular* or *distorted geometry*. The order of repulsions between electron pairs is as follows :

Lone pair – Lone pair > Lone pair-Bond pair > Bond pair-Bond pair.

(5) The exact shape of the molecule depends upon the total number of electron pairs present around the central atom.

Based on VSEPR theory, the shapes of molecules containing 2, 3, 4, 5 or 6 electron pairs around the central atom, all of which may be bond pairs only or some of these may be bond pairs and the remaining may be lone pairs are given in Table 6.6 on next page alongwith examples of each type. The detailed discussion of the examples is given in section 6.25.

6.24. Hybridisation (Valence Bond Approach)

No doubt VSEPR theory is able to explain the shapes of simple molecules but is unable to predict the exact shape in a number of cases. Moreover talking of the direction of electron pairs does not seem to be very rational. It was only with the advent of Valence Bond Theory that the shapes of molecules could be explained more precisely. As already explained, according to Valence Bond theory, a covalent bond is formed by the overlap of half-filled atomic orbitals. The direction of overlap gives the direction of the bond. However in applying this theory, a difficulty was faced in a number of cases as explain below :

As a covalent bond is formed by the overlap of a half-filled atomic orbital, therefore the covalency of the element should be equal to the number of half-filled orbitals present in an atom of that element. However, on the basis of this concept, the formation of many compounds such as those of beryllium, boron and carbon could not be explained. Now let us have a look at this problem.

The electronic configurations of beryllium, boron and carbon in the ground state are as follows :

Element	**Atomic Number**	**Electronic Configuration**
Be	4	$1s^2, 2s^2$
B	5	$1s^2, 2s^2, 2p_x^1$
C	6	$1s^2, 2s^2, 2p_x^1\ 2p_y^1$

On the basis of these configurations, we may conclude that beryllium, boron and carbon should possess zero, one and two covalenceis respectively because beryllium has no half-filled atomic orbital, boron has one and carbon has two. But actually beryllium has a covalency of two as in the case of

Contd. on page 6/35

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*It was this improvement which was put forward by Nyholm and Gillespie in 1957. They pointed out that there is an important difference between lone pair and bond pair. Whereas the lone pair is localized on the atom, the bond pair is shared between two atoms. As a result, a lone pair occupies more space and hence causes greater repulsion, giving the order *lp—lp > lp—bp > bp—bp*.

TABLE 6.6. Shapes (Geometry) of molecules containing bond pairs only or bond pairs and lone pairs.

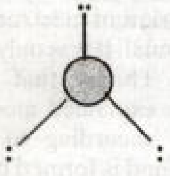
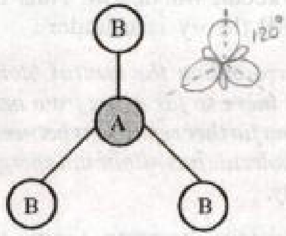
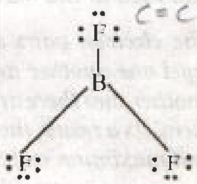
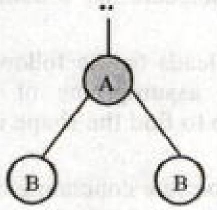
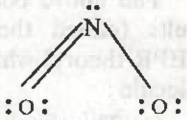
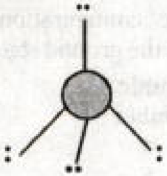
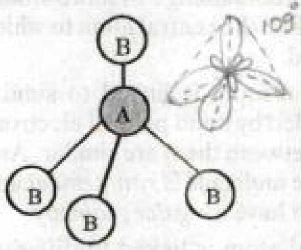
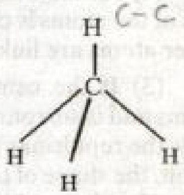
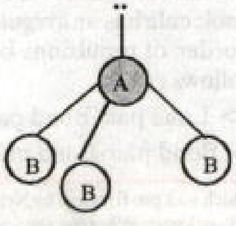
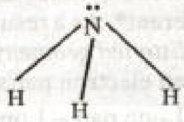
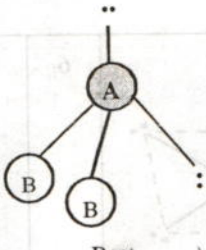
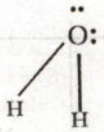
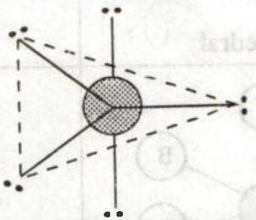
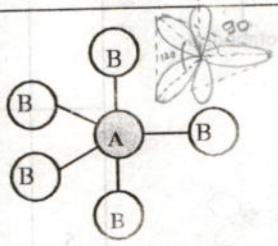
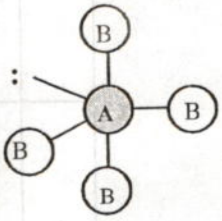
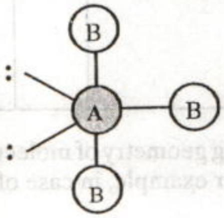
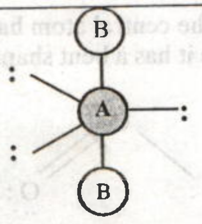
Total No. of electron pairs	Geometry of the electron pairs	Bond pairs	Lone Pairs	Geometry of the molecule	Examples
2 SP	 Linear	2	0	 Linear 180°	$\ddot{O}=C=\ddot{O}$ Be C≡C
3 Sp²	 Triangular planar	3	0	 120° Triangular planar	 B C=C
		2	1	 Bent	
4 Sp³	 Tetrahedral	4	0	 109° Tetrahedral	 C–C
		3	1	 Trigonal pyramidal	 & $[SnCl_3]^-$

TABLE CONTINUED

		2	2	 Bent	
5 sp^{3}d	 Trigonal bipyramidal d$_{z^2}$	5	0	 Trigonal bipyramidal	PCl_5
		4	1	 See saw	SF_4
		3	2	 T-shaped	ClF_3
		2	3	 Linear	XeF_2

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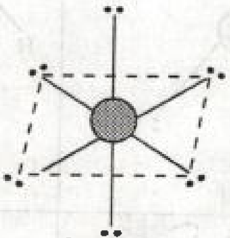
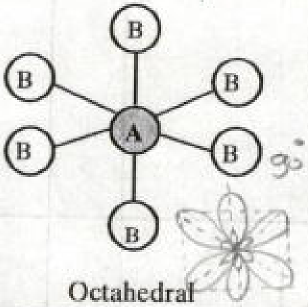
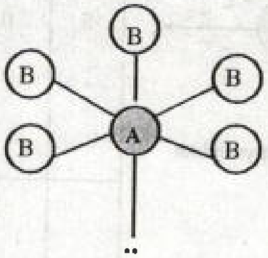
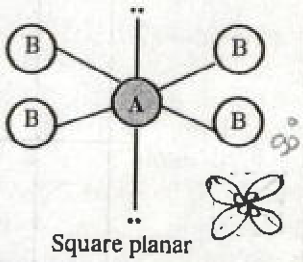
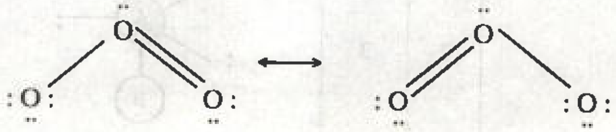
6 Sp^3d^2	 Octahedral dx^2-y^2 dz^2	6	0	 Octahedral	SF_6
		5	1	 Square pyramidal	ClF_5
dsp^2	$d_{x^2-y^2}$ s two p	4	2	 Square planar	XeF_4

Note. In predicting geometry of molecules containing double bond, the double bond is considered as one electron pair. For example, in case of ozone, its two resonating structures are

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

In each structure, the central atom has one lone pair and two bond pairs (counting double bond as one bond pair). Hence it has a bent shape



BeF_2, boron has a covalency of three as in BF_3 whereas carbon has a covalency of four, *e.g.*, in CH_4, CCl_4, CO_2 etc.

To overcome the above problem, it was suggested that one paired electron becomes unpaired and jumps to an empty orbital without consuming excessive energy. Let us, for example, consider the case of carbon. Its atomic number is 6 and so its configuration in the ground state is

$_6C$ .... $1s^2$, $2s^2\ 2p_x^1\ 2p_y^1$ (Ground state)

Thus, it has two unpaired electrons in the ground state. So it should form two bonds only. But actually carbon shows a covalency of 4. To explain this, it is suggested that an electron from 2*s* orbital jumps to 2*p* orbital and so the configuration of carbon in the excited state is

$_6C$ .... $1s^2$, $2s^1\ 2p_z^1\ 2p_y^1$, $2p_z^1$ (Excited state)

Thus now carbon has four unpaired electrons thereby explaining tetravalent nature of carbon. Its one *s* and three *p* orbitals can overlap with the half-filled orbitals of reacting atoms, forming four covalent bonds. But covalent bond formed by 2*s* orbital of carbon should differ in energy from the bonds obtained by the three *p* orbitals. However, experimental data clearly show that all the four bonds of carbon are same in energy. Moreover, the three bonds formed by 2*p* orbitals should be at 90° to each other and the fourth formed from 2*s* orbital may have any direction. However, this is actually not so. Hence a new concept was introduced to explain this abnormal behaviour of carbon. According to this concept, all the four orbitals of carbon having unpaired electrons and possessing slightly different energies mix up their energies and then redistribute it in four equal quantities thus giving rise to four new orbitals each having the same amount of energy. This new concept was referred as hybridisation. Thus

Hybridisation is defined as the mixing of the atomic orbitals belonging to the same atom but having slightly different energies so that a redistribution of energy takes place between them resulting in the formation of new orbitals of equal energies and identical shapes. The new orbitals thus formed are known as hybrid orbtials.

The shape of a hybrid orbital (made from *s* and *p* orbitals) is like that of *p* orbital except that the two lobes are unequal in size, *i.e.*, there is one small lobe opposite to a big lobe on the other side as shown in Fig. 6.26.

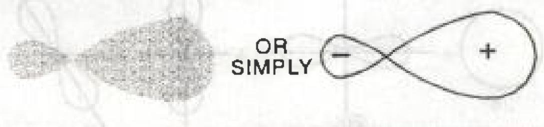


FIGURE 6.26. Representation of a hybrid orbital.

Note carefully ***that the energy required for excitation of electrons becomes available when the combining atoms approach each other because energy is released when combining atoms approach each other. That is why hybridisation never takes place in isolated atoms but occurs only at the time of bond formation.***

Some Important Points about Hybridisation :

(*i*) Only those orbitals which have approximately equal energies and belong to the same atom or ion can undergo hybridisation.

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

(*iii*) It is not necessary that all the half-filled orbitals must participate in hybridisation. Similarly, it is not necessary that only half-filled orbitals should participate in hybridisation. Even completely filled orbitals with slightly different energies can also participate.

(*iv*) Hybridisation never takes place in isolated atoms but it occurs only at the time of bond formation.

(*v*) Type of hybridisation indicates the geometry of molecules. One can tell the shape of a molecule by knowing the kind of hybridisation involved.

(*vi*) The bigger lobe of the hybrid orbital always has +ve sign while the smaller lobe on the opposite side has a −ve sign.

Types of Hybridisation.

1. Diagonal or sp hybridisation.

When one s and one p orbital belonging to the same main shell of an atom mix together to form two new equivalent orbitals, the type of hybridisation is called sp hybridisation or diagonal hybridisation. The new orbitals formed are called sp hybrid orbitals.

They are collinear with an angle of 180° as shown in Fig. 6.27.

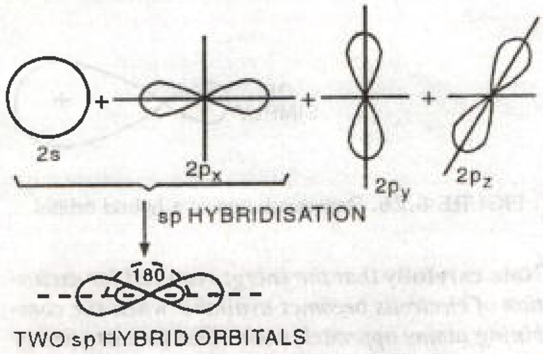


FIGURE 6.27. Diagonal or sp hybridization.

Each of the hybrid orbitals formed has 50% *s*-character and 50% *p*- character. The remaining two p-orbitals which do not participate in hybridisation remain as such. If these are half-filled, they may form bonds with other atoms having half-filled atomic orbitals.

EXAMPLES. A few compounds in which *sp* hybridisation is involved are

(*i*) All compounds of beryllium like BeF_2, BeH_2 etc.

(*ii*) All compounds of carbon containing C≡C triple bond like acetylene (C_2H_2).

These will be discussed later under 'Shapes of molecules'.

2. Trigonal or sp² hybridisation.

When one s and two p orbitals of the same shell of an atom mix to form three new equivalent orbitals, the type of hybridisation is called sp² hybridisation or trigonal hybridisation. The new orbitals formed are called sp² hybrid orbitals.

All the three hybrid orbitals remain in the same plane making an angle of 120° with one another as represented in Fig. 6.28.

Each of the hybrid orbitals formed has 1/3rd *s*-character (33%) and 2/3rd *p*-character (67%). The non-participating *p*-orbital, if half- filled, can form bond with other atoms having half-filled orbitals.

EXAMPLES. A few compounds in which sp^2 hybridisation takes place are

(*i*) All compounds of boron, *e.g.*, BF_3, BH_3 etc.

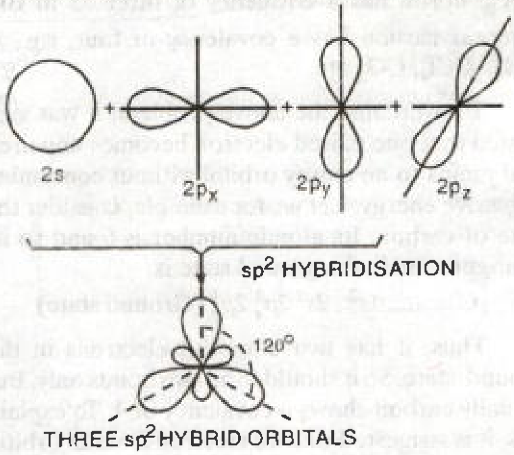


FIGURE 6.28. Trigonal or sp² hybridization.

(*ii*) All compounds of carbon containing C=C double bond.

These are discussed later under 'Shapes of molecules'.

3. Tetrahedral or sp³ hybridisation.

When one s and three p-orbitals belonging to the same shell of an atom mix together to form four new equivalent orbitals, the type of hybridisation is called sp³ or tetrahedral hybridisation. The new orbitals are called sp³ or tetrahedral orbitals.

These are directed towards the four corners of a regular tetrahedron and make an angle of 109° 28′ with one another as represented in Fig. 6.29.

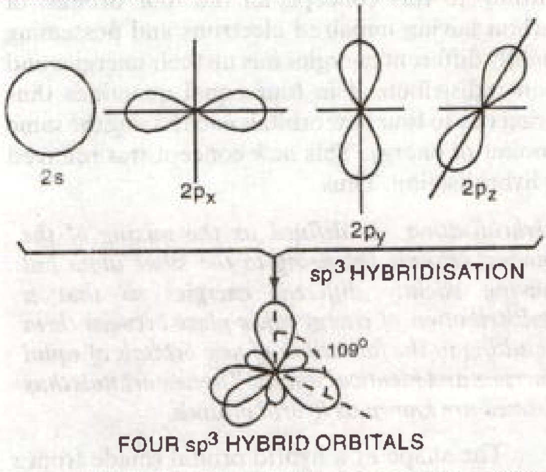


FIGURE 6.29. Tetrahedral or sp³ hybridization.

Each sp^3 hybrid orbital has 25% *s*-character and 75% *p*- character.

EXAMPLES. A few compounds in which sp^3 hybridisation occurs are methane (CH_4), ethane (C_2H_6) etc., *i.e.*, all compounds of carbon containing C – C single bonds only. These are discussed in detail in the next section under the 'Shapes of molecules'.

It is interesting to mention here that the size of *sp*-hybrid orbital is smaller than that of sp^2 hybrid orbital which in turn is smaller than that of sp^3 hybrid orbital.

6.25. Directional Properties of Bonds and Geometry or Shapes of Molecules

As already discussed, ionic bond is non-directional. Hence the structure of an ionic compound is determined by the relative size of the ions. However a covalent bond is directional. This is because a covalent bond is formed by the overlap of half-filled orbitals (hybridised or unhybridised). The direction of overlap gives the direction of the bond. Further, it may be pointed out that a hybridised orbital has greater directional character than p-orbital because p-orbital has equal sized lobes with equal electron density in both the lobes whereas a hybridized orbital has greater electron density on one side. Thus, in case of molecules containing three or more atoms, one of the atoms is the central atom and the other atoms are linked to it in definite directions.

A particular arrangement obtained by bonding a number of atoms in definite directions to the central atom of a molecule is called the geometry or shape of the molecule.

The geometry or shape of a molecule (as found by experimental methods) can be explained on the basis of either of the following :

(*i*) *Valence Shell Electron Pair Repulsion Theory (VSEPR Theory)*

(*ii*) *Hybridisation*

The shapes of a few molecules on the basis of hybridization as well as VSEPR theory are briefly described below :

A. SHAPES OF MOLECULES CONTAINING BOND PAIRS ONLY

(1) Shape of Beryllium fluoride (BeF_2) molecule :

***(a)* On the basis of hybridisation**

Atomic number of Be = 4

Its electronic configuration in the ground state is $1s^2\,2s^2$.

The electronic configuration in the excited state is $1s^2\,2s^1\,2p_x^1$.

One 2*s* and one 2*p* orbital undergo *sp* hybridisation to form two half-filled *sp* hybrid orbitals which are oriented at an angle of 180°. They overlap with the half-filled orbitals of two fluorine atoms to give a **linear** shape as shown in Fig. 6.30.

***(b)* On the basis of VSEPR theory.** In BeF_2, the central atom is Be which has two valence electrons. It shares these electrons with two fluorine atoms, *i.e.* its Lewis structure is

$$:\overset{\cdot\cdot}{\underset{\cdot\cdot}{F}}\ :\ Be\ :\ \overset{\cdot\cdot}{\underset{\cdot\cdot}{F}}:$$

Thus Be atom is surrounded by two bond pairs only. According to VSEPR theory, these bond pairs repel each other and go as far apart as possible so that there are no further repulsions. This is possible only when they take up positions at an angle of 180° to each other as shown above, thereby giving it a **linear** shape.

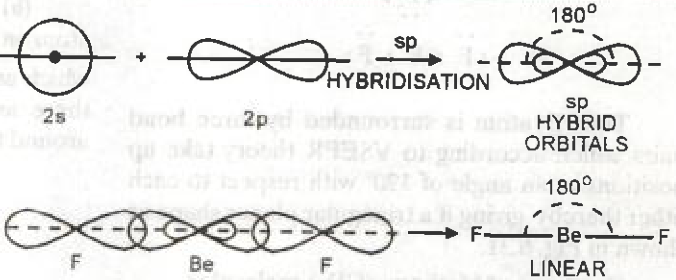


FIGURE 6.30. Formation of sp hybrid orbitals and shape of BeF_2.

(2) Shape of Boron trifluoride (BF_3) molecule :

***(a)* On the basis of hybridisation**

Atomic number of B = 5

Its electronic configuration in the ground state is $1s^2\,2s^2\,2p_x^1$.

The electronic configuration in the excited state is $1s^2\,2s^1\,2p_x^1\,2p_y^1$

One 2*s* and two 2*p* orbitals undergo sp^2 hybridisation to form three half-filled sp^2 hybrid orbitals which are planar and oriented at an angle of 120° to each other. These overlap with half-filled orbitals of three fluorine atoms to form BF_3 which, therefore, has **triangular planar** shape as shown in Fig. 6.31.

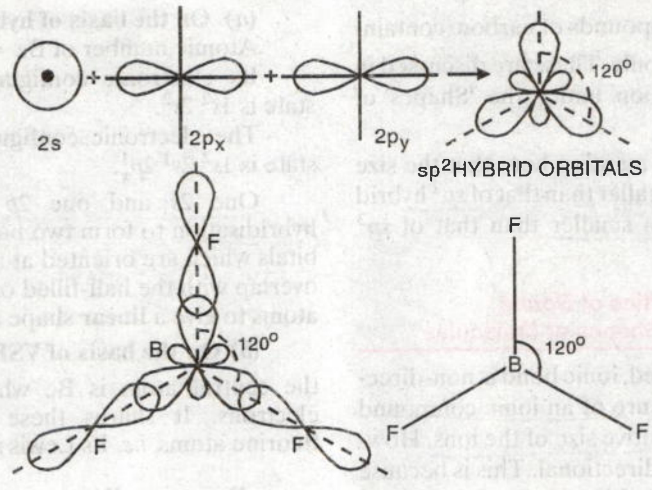


FIGURE 6.31. Formation of sp^2 hybrid orbitals and shape of BF_3.

(*b*) On the basis of VSEPR theory. In BF_3, the central atom is B which has three valence electrons. It shares these electrons with three fluorine atoms *i.e.* its Lewis structure is

$$\begin{array}{c} :\overset{\cdot\cdot}{\underset{\cdot\cdot}{F}}: \\ :\overset{\cdot\cdot}{F}:B:\overset{\cdot\cdot}{F}: \end{array}$$

Thus B atom is surrounded by three bond pairs which according to VSEPR theory take up positions at an angle of 120° with respect to each other thereby giving it a triangular planar shape as shown in Fig. 6.31.

(3) Shape of Methane (CH_4) molecule :

(*a*) On the basis of hybridisation.

Atomic number of C = 6

Its electronic configuration in the ground state is $1s^2\,2s^2\,2p_x^1\,2p_y^1$

The electronic configuration in the excited state is $1s^2\,2s^1\,2p_x^1\,2p_y^1\,2p_z^1$

One 2*s* and three 2*p* orbitals undergo sp^3 hybridisation to form four sp^3 hybrid orbitals which are arranged tetrahedrally at an angle of 109° 28′ to each other.

The four sp^3 hybrid orbitals overlap with the half- filled 1*s* orbitals of four H-atoms, forming CH_4 as represented in Fig. 6.32. Thus CH_4 is a **tetrahedral** molecule with each H-C- H angle equal to 109° 28′ (≈ 109·5°).

(*b*) On the basis of VSEPR theory. Central atom in CH_4 is C. It has four valence electrons which are shared with four hydrogen atoms. Thus there are four bond pairs of electrons present around the central atom (carbon) as follows :

$$\begin{array}{c} H \\ \bullet\bullet \\ H\ :\ C\ :\ H \\ \bullet\bullet \\ H \end{array}$$

Now according to VSEPR theory, these four electron pairs will repel each other and thus move so far apart that there are no further repulsions between them. The only shape possible is tetrahedral as shown in Fig. 6.32.

Some other examples of molecules/ions having tetrahedral shapes are CCl_4, SiF_4, SiH_4, NH_4^+, BF_4^- etc.

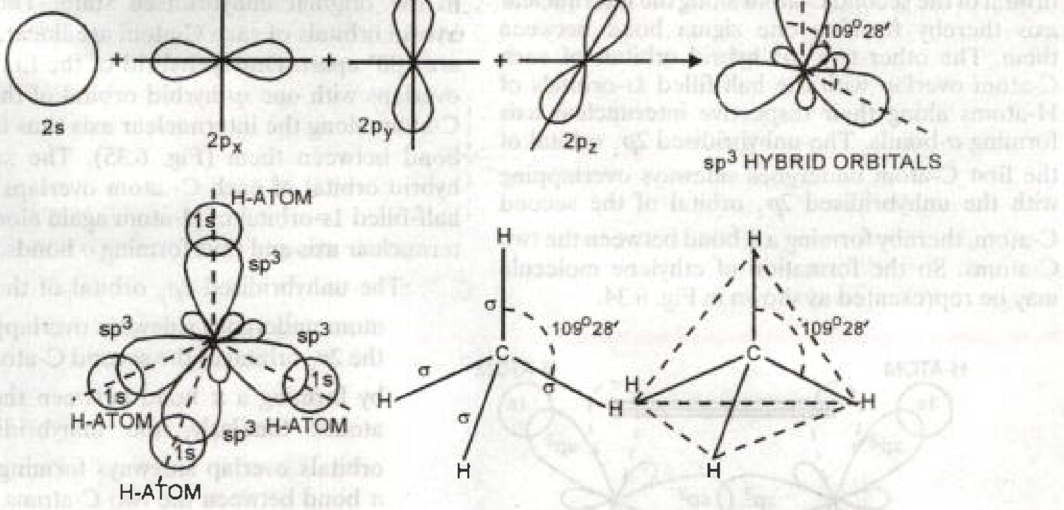


FIGURE 6.32. Formation of CH_4 molecule.

(4) Shape of Ethane (C_2H_6) molecule : In the formation of ethane molecule, each carbon atom undergoes sp^3 hybridisation, thus forming four sp^3 hybrid orbitals directed towards the corners of a tetrahedron and inclined to each other at an angle of 109°28′. One sp^3 hybrid orbital of the first carbon atom undergoes overlapping with one sp^3 hybrid orbital of the second carbon atom along the internuclear axis, thus forming a σ bond between them. The remaining three sp^3 hybrid orbitals of each carbon atom undergo overlapping with the half-filled 1*s*-orbitals of H-atoms, each along the internuclear axis and hence forming a σ bond. Thus the complete picture may be represented as shown in Fig. 6.33

Obviously, the molecule has a regular geometry.

The various bond parameters are found to be as follows :

(*i*) C-C bond length = 154 pm

(*ii*) Each C-H bond length = 110 pm

(*iii*) Each H-C-C

or H-C-H bond angle = 109°28′

(*iv*) C-C bond dissociation energy

= 348 kJ mol^{-1}.

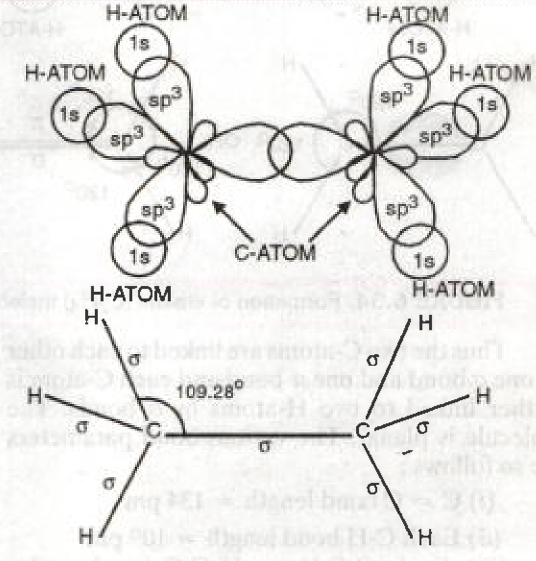


FIGURE6.33. Formation of ethane molecule.

(5) Shape of Ethylene (C_2H_4) molecule : The electronic configuration of C-atom in the excited state is : $_6C = 1s^2\, 2s^1\, 2p_x^1\, 2p_y^1\, 2p_z^1$

In the formation of ethylene molecule, each C-atom undergoes sp^2 hybridisation, thus leaving one $2p_z$ orbital in the original state, *i.e.*, in the unhybridised state. The three sp^2 hybrid orbitals of each C-atom are planar and are inclined to each other at an angle of 120°. One sp^2 hybrid orbital of the first C-atom overlaps with one sp^2 hybrid orbital of the second C-atom along the internuclear axis thereby forming one sigma bond between them. The other two sp^2 hybrid orbitals of each C-atom overlap with the half-filled $1s$-orbitals of H-atoms along their respective internuclear axis forming σ-bonds. The unhybridised $2p_z$ orbital of the first C-atom undergoes sideways overlapping with the unhybridised $2p_z$ orbital of the second C-atom, thereby forming a π bond between the two C-atoms. So the formation of ethylene molecule may be represented as shown in Fig. 6.34.

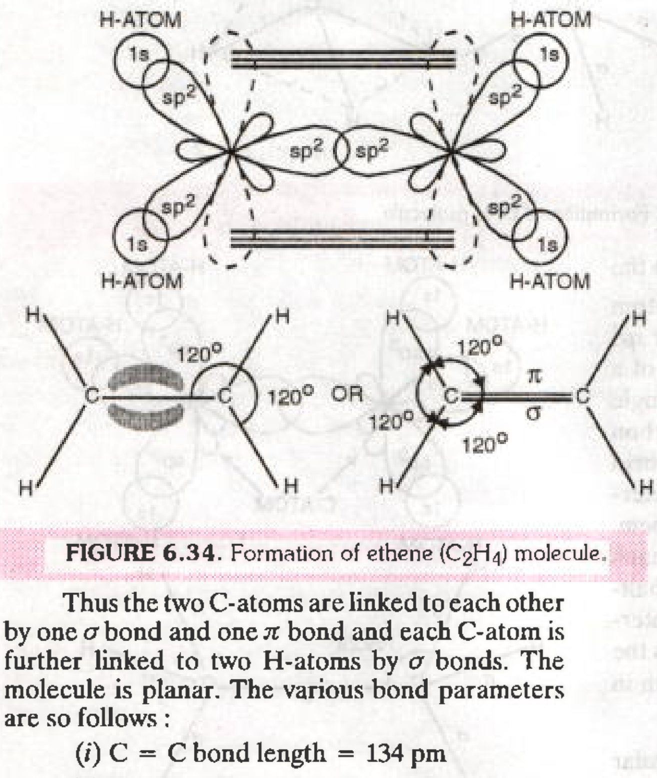


FIGURE 6.34. Formation of ethene (C_2H_4) molecule.

Thus the two C-atoms are linked to each other by one σ bond and one π bond and each C-atom is further linked to two H-atoms by σ bonds. The molecule is planar. The various bond parameters are so follows :

(*i*) C = C bond length = 134 pm

(*ii*) Each C-H bond length = 109 pm

(*iii*) Each C-C-H or H-C-C bond angles = 120°

(*iv*) Total C = C bond dissociation energy = 614 kJ mol^{-1}.

Out of 614 kJ, the bond dissociation energy for σ bond is 348 kJ (as already mentioned). Therefore, the bond dissociation energy for π bond is 614 – 348 = 266 kJ/mole. Hence π bond is a weaker bond. This is the reason for high reactivity of compounds containing π bonds.

(6) Shape of Acetylene (C_2H_2) molecule : In the formation of acetylene molecule, each C-atom undergoes *sp* hybridisation leaving two $2p$ orbitals in the original unhybridised state. The two sp hybrid orbitals of each C-atom are linear, *i.e.*, they are 180° apart. One *sp* hybrid of the first C-atom overlaps with one *sp* hyrbid orbital of the second C-atom along the internuclear axis thus forming σ bond between them (Fig. 6.35). The second *sp* hybrid orbital of each C- atom overlaps with the half-filled 1s-orbital of H-atom again along the internuclear axis and thus forming σ bonds.

The unhybridised $2p_y$ orbital of the first C-atom undergoes sideways overlapping with the $2p_y$ orbital of the second C-atom, thereby forming a π bond between the two C-atoms. Similarly, the unhybridised $2p_z$ orbitals overlap sideways forming another π bond between the two C-atoms. Thus all the carbon and hydrogen atoms are linear and there is electron cloud above and below, in the front and at the back of the C – C axis. In other words, there is electron cloud all around the internuclear axis thus giving a cylindrical shape as represented in Fig. 6.35.

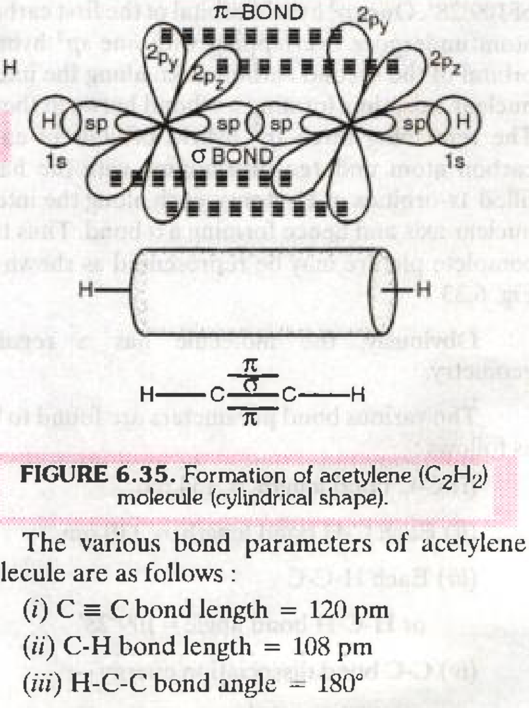


FIGURE 6.35. Formation of acetylene (C_2H_2) molecule (cylindrical shape).

The various bond parameters of acetylene molecule are as follows :

(*i*) C ≡ C bond length = 120 pm

(*ii*) C-H bond length = 108 pm

(*iii*) H-C-C bond angle = 180°

(*iv*) Total C≡C bond dissociation energy = 811 kJ mol^{-1}

(7) Shape of PF_5 molecule. In PF_5, the central atom, phosphorus, has the ground state electronic configuration $1s^2\,2s^2\,2p^6\,3s^2\,3p_x^1\,3p_y^1\,3p_z^1$. One of the 3s electron gets promoted to 3d orbital giving the electronic configuration $1s^2\,2s^2\,2p^6\,3s^1\,3p_x^1\,3p_y^1\,3p_z^1\,3d^1$. Thus it involves sp^3d hybridisation (Fig. 6.36).

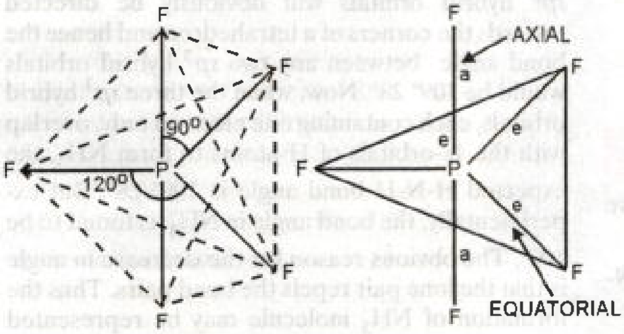
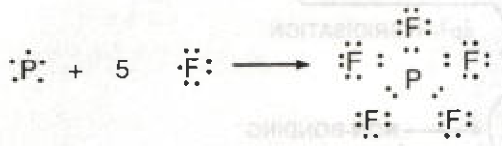


FIGURE 6.36. Trigonal bipyramidal geometry of PF_5.

Alternatively, the central P-atom has 5 valence electrons. As a result, it is surrounded by five bond pairs of electrons.



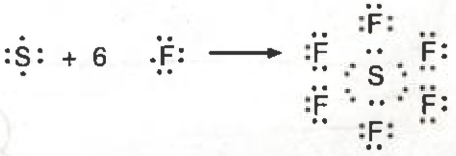
According to VSEPR theory, for PF_5 to have minimum energy, the bond pairs of electrons should be as far apart as possible from each other. This is possible only if the molecule acquires a **trigonal bipyramidal shape.**

In this structure, three of the fluorine atoms lie in the same plane as phosphorus atom and are called **equatorial** fluorine atoms and the bonds formed are called **equatorial bonds.** The other two fluorine atoms lie at right angle to the plane of equatorial bonds and are known as **axial** fluorine atoms and the bonds formed by them are called **axial bonds.**

Bond lengths and Bond angles in PF_5. Electron diffraction studies of PF_5 gas show that the equatorial bonds are at angle of 120° with each other whereas axial bonds make an angle of 90° with the equatorial bonds. Further, these studies show that axial P – F bonds are slightly longer than equatorial P – F bonds (Bond lengths : P – F axial = 158 pm, P – F equatorial = 153 pm). However NMR (Nuclear Magnetic Resonance) studies show that all the five F atoms are equivalent and can exchange their positions* and hence all the five P – F bonds have the same length. The reason for the difference in the two studies is on account of the fact that electron diffraction gives instantaneous picture of the molecule whereas NMR takes time more than the time required for the interchange of axial and equatorial F atoms.

Other examples. Similar geometry is expected for PCl_5 and $SbCl_5$ molecules. However in PCl_5, axial P – Cl bonds (bond length = 219 pm) are longer than equatorial P – Cl bonds (bond length = 204 pm).

(8) Shape of sulphur hexafluoride (SF_6). In SF_6, the central atom, sulphur, has the ground state electronic configuration $1s^2\,2s^2\,2p^6\,3s^2\,3p_x^2\,3p_y^1\,3p_z^1$ and F has $1s^2\,2s^2\,2p_x^2\,2p_y^2\,2p_z^1$. One of the 3s elecrtrons as well as 3p electron get promoted to 3d orbitals giving the electronic configuration $1s^2\,2s^2\,2p^6\,3s^1\,3p_x^1\,3p_y^1\,3p_z^1\,3d^1\,3d^1$. Thus it involves sp^3d^2 hybridisation. Alternatively, it has 6 electrons in the valence shell. As a result, the central atom is surrounded by six bond pairs of electrons in the valence shell.



According to VSEPR theory, for SF_6 to have minimum energy, the bond pairs of electrons should be as far apart as possible from each other. This is possible only if the molecule acquires a **regular octahedral** geometry (Fig. 6.37).

If SF_6, four S – F bonds are in the same plane at right angles to one another and are directed towards the four corners of a square. The other two F atoms lie at right angle above and below the plane of F atoms.

SF_6 molecule is a symmetrical molecule and, therefore, is stable and far less reactive.

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*The interchange of axial and equatorial positions is called 'pseudorotation'.

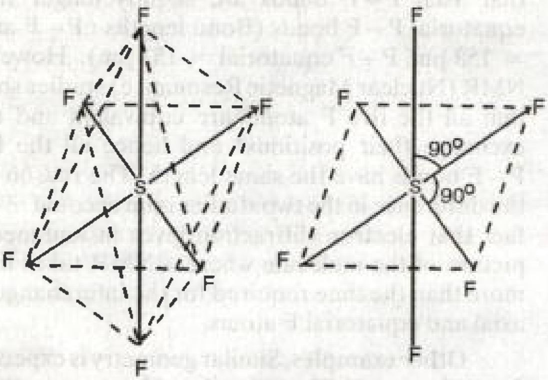


FIGURE 6.37. Octahedral geometry of SF_6.

Other examples. TeF_6 is also expected to have a regular octehedral geometry.

B. SHAPES OF MOLECULES CONTAINING BOND PAIRS AS WELL AS LONE PAIRS

(9) Shape of Ammonia (NH_3) molecule :

Atomic number of N = 7

∴ Its electronic configuration is

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

One 2*s* and three 2*p* orbitals undergo sp^3 hybridisation forming four sp^3 hybrid orbitals out of which three contain one electron each and take part in bond formation and the fourth sp^3 hybrid orbital contains a lone pair of electrons and hence cannot participate in the bond formation. The four sp^3 hybrid orbitals will obviously be directed towards the corners of a tetrahedron and hence the bond angle between any two sp^3 hybrid orbitals would be 109° 28′. Now, when the three sp^3 hybrid orbitals, each containing one electron only, overlap with the 1s-orbitals of H-atoms to form NH_3, the expected H-N-H bond angle is 109° 28′. But experimentally, the bond angle in NH_3 is found to be 107°. The obvious reason for the decrease in angle is that the lone pair repels the bond pairs. Thus the formation of NH_3 molecule may be represented diagrammatically as shown in Fig. 6.38.

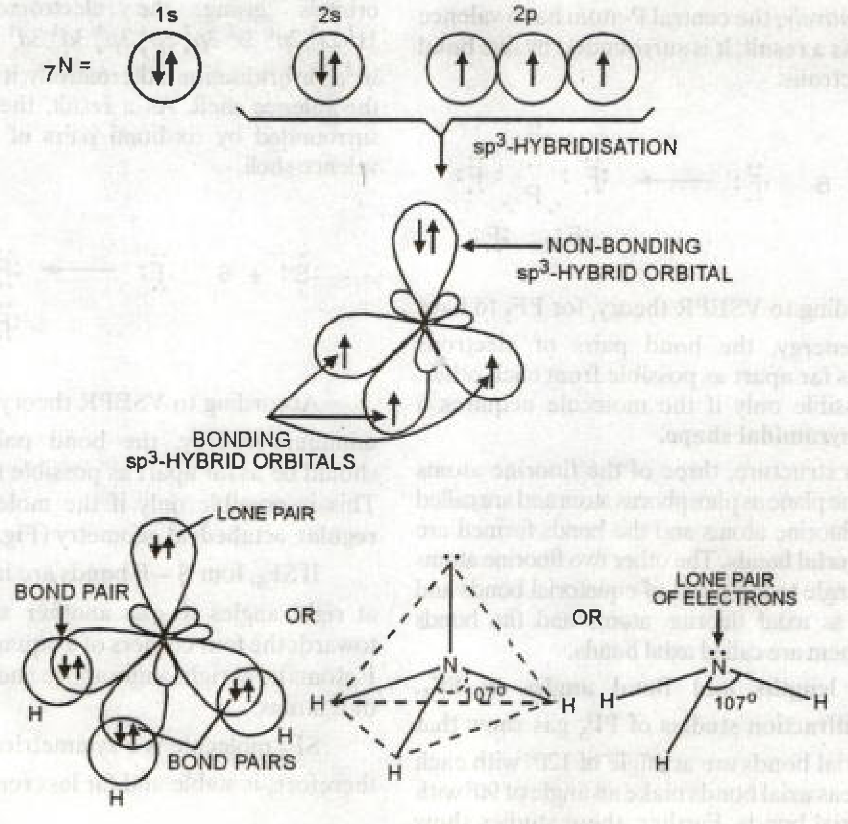


FIGURE 6.38. Formation of ammonia (NH_3) molecule.

Such a shape is known as **trigonal (or triangular) pyramid** in which the three H-atoms form the triangular base of the pyramid with N-atom at the apex. The same applies to molecules like PCl_3, NF_3 and H_3O^+.

(10) Shape of water (H_2O) molecule : The shape of H_2O molecule can be explained exactly in the same way as in case of NH_3 molecule.

Atomic number of Oxygen = 8

∴ Its electronic configuration is

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

One 2*s* and three 2*p* orbitals undergo sp^3 hybridisation forming four sp^3 hybrid orbitals out of which two contain one electron each and the other two contain a pair of electrons (*i.e.*, lone-pair) each. As usual, the four sp^3 hybrid orbitals thus formed are directed towards the corners of a tetrahedron and hence the bond angle between any two sp^3 hybrid orbitals would be 109°28′. Now when the two sp^3 hybrid orbitals containing one electron each, overlap with the half-filled 1*s* orbitals of H-atoms to form H_2O, the expected H-O-H bond angle is 109°28′. But experimentally the bond angle is found to be 104·5°. The reason for the still lesser bond angle in H_2O than in NH_3 is that in this case there are two lone pairs of electrons present which repel the bond pairs. Thus in this case the repulsions are more than those in the case of NH_3 molecule. The formation of H_2O molecule may be represented as shown in Fig. 6.39. Thus water is **V-shaped or bent molecule.**

HF molecule is linear since it has only two atoms though in this case also, four electron pairs (one bond pair and three lone pairs) form tetrahedral geometry.

Some other examples of molecules/ions having shape similar to that of H_2O are SO_2, F_2O, NH_2^-, SCl_2 etc.

(11) Shape of SF_4 molecule. This is an example of a molecule in which the effect of lone pair has a great significance in deciding the shape of the molecule.

Atomic number of the central atom (S) = 16. Its electronic configuration is

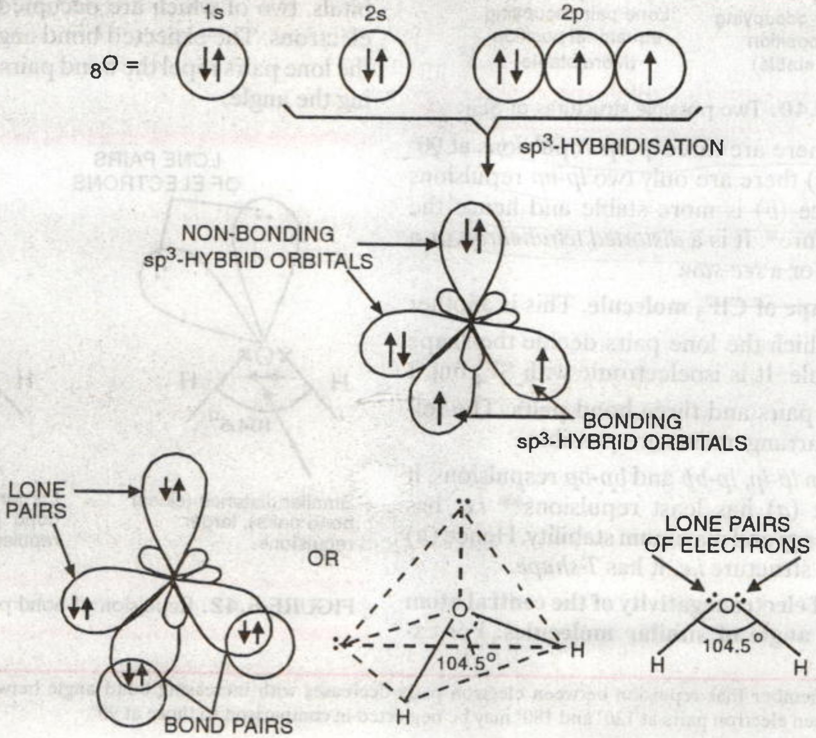


FIGURE 6.39. Formation of water (H_2O) molecule.

$1s^2\,2s^2\,2p^6\,3s^2\,3p_x^2\,3p_y^1\,3p_z^1$

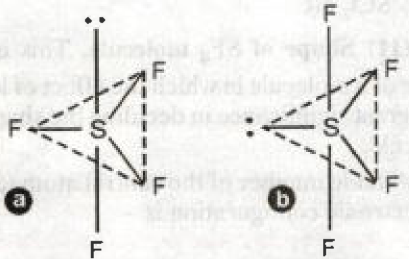
or in the excited state, it is

$1s^2\,2s^2\,2p^6\,3s^2\,3p_x^1\,3p_y^1\,3p_z^1\,3d^1$

It undergoes sp^3d hybridisation to form five hybrid orbitals to give a trigonal bipyramidal arrangement in which one hybrid orbital occupies a lone pair and the remaining four contain one electron each which are shared with those of F-atoms.

In terms of VSEPR model, in SF_4, S atom has 5 electron pairs around it *i.e.* 4 bond pairs and one lone pair. Hence their arrangement should be trigonal bipyramidal.

Depending upon the position occupied by lone pair, two possible structures of SF_4 are :



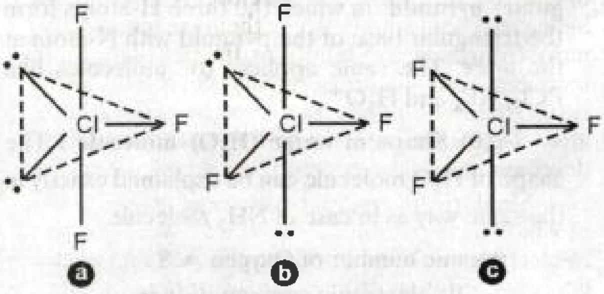
Lone pair occupying axial position (Less stable)

Lone pair occupying equatorial position (More stable)

FIGURE 6.40. Two possible structures of SF_4.

In (*a*), there are three *lp-bp* repulsions at 90° whereas in (*b*) there are only two *lp-bp* repulsions at 120°. Hence (*b*) is more stable and hence the correct structure*. It is a *distorted tetrahedron* or a *folded square* or a *see-saw*.

(12) Shape of ClF_3 molecule. This is another example in which the lone pairs decide the shape of the molecule. It is isoelectronic with SF_4 but it has two lone pairs and three bond pairs. The following three arrangements are possible :



(Most stable)

FIGURE 6.41. Three possible structures of ClF_3.

Based on *lp-lp, lp-bp* and *bp-bp* respulsions, it is found that (*a*) has least repulsions** *i.e.* has minimum energy and maximum stability. Hence (*a*) is the correct structure *i.e.* it has *T-shape*.

Effect of electronegativity of the central atom on the bond angle of similar molecules. For example, in the hydrides of group 16 (all of which have V-shape *i.e.* they are bent molecules), the bond angles *decrease* as follows :

H_2O	H_2S	H_2Se	H_2Te
104·5°	92·5°	91·0°	90·5°

This decrease may be explained as follows :

The outer shell electronic configuration of O, S, Se and Te is $ns^2\,np^4$ or $ns^2\,np_x^2\,np_y^1\,np_z^1$. They undergo sp^3 hybridisation forming four hybrid orbitals, two of which are occupied by lone pairs of electrons. The expected bond angle is 109°28′. But the lone pairs repel the bond pairs thereby decreasing the angle.

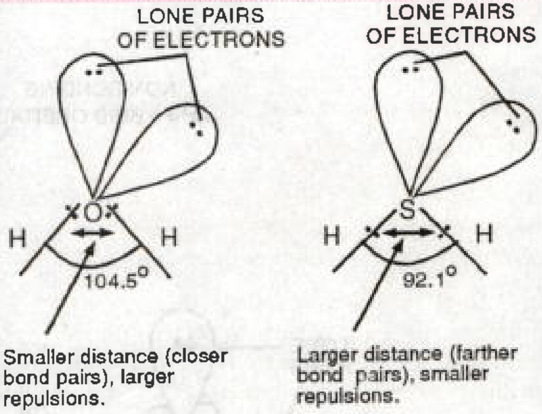


FIGURE 6.42. Repulsion of bond pairs and lone pairs.

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*Also remember that repulsion between electron pairs decreases with increasing bond angle between them. Therefore repulsions between electron pairs at 120° and 180° may be neglected in comparison to those at 90°.

**In (a), $lp-lp = 0, lp-bp = 4, bp-bp = 2$

In (b), $lp-lp = 1, lp-bp = 3, bp-bp = 2$

In (c), $lp-lp = 0, lp-bp = 6, bp-bp = 0$

Compared with (b), (a) has no $lp-lp$ repulsions. Compared with (c), (a) has less $lp-bp$ repulsions.

Due to smaller size and high electronegativity of O-atom, the bond pairs are closer to O-atom and hence the repulsions between them are large. As we move from oxygen to tellurium, the size of the atom increases and electronegativity decreases. As a result, the bond pairs move away from the central atom. Hence the repulsions between the bond pairs decrease and so the bond angle also decreases.

Similarly, in case of hydrides of group 15 (all of which have pyramidal shape with one lone pair of electrons on the central atom), the bond angles decrease as follows :

NH_3	PH_3	AsH_3	BiH_3
107·5°	93·4°	91·5°	91·2°

Conclusion. ***In similar molecules, as the electronegativity of the central atom decreases, and the size increases, the bond angle decreases.***

Effect of electronegativity of the surrounding atom on the bond angle of similar molecules. For example, in the trihalides of phosphorus (all of which have pyramidal shape), the bond angles *increase* as follows :

PF_3	PCl_3	PBr_3	PI_3
97°	100°	101·5°	102°

This is evidently due to the fact that due to high electronegativity of F, bond pair of electrons is more attracted towards F *i.e.* it lies away from the central atom. As electronegativity decreases from F to I, the bond pairs are closer to the central atom and the repulsions between the bond pairs increase and so the bond angle also increases.

For the same reason, the bond angle in F_2O is smaller than that in H_2O.

Conclusion. ***In similar molecules, as the electronegativity of the surrounding atom decreases, the bond angle increases.***

Note. (*i*) For molecules or ions having regular geometry, the change in the electronegativity of the central atom or the surrounding atom has no effect on the bond angle. For example, BF_3, BCl_3, BBr_3, $AlCl_3$ etc. all have the same bond angle viz 120°. Similarly, CH_4, CCl_4, NH_4^+ etc. all have the same bond angle viz. 109°28′.

(*ii*) Bond angles may vary due to certain other factors also *e.g.* bond angle of NH_3 is greater than that of NF_3 but bond angle of PH_3 is less than that of PF_3 (See Page 6/67).

6.26. Co-ordinate or Dative Bond

Perkins in 1921, suggested a third possible way by which atoms can combine and form a molecule to account for the structures of certain compounds such as sulphur trioxide, sulphuric acid, nitric acid etc.

It was assumed that certain atoms which have complete octets can donate their valence electrons which are not involved in the bond formation, to other atom/atoms which are short of electrons. These donated electrons are, therefore, lone pairs of electrons and are shared by both the atoms.

When in the formation of a bond, the electron pair (lone pair) is donated by one atom but shared by both the atoms so as to complete their octets, the bond formed is called co-ordinate bond or dative bond.

Thus whereas in case of covalency, the shared pair of electrons has equal contribution from both the combining atoms, in this case shared pair comes from only one atom, and this atom is termed as **donor** and the other atom as **acceptor**. This bond is represented by an arrow pointing from the donor to the acceptor. Compounds having this linkage are known as co-ordinate compounds. Since this bond has some polar character, it is also known as **dative or semi-polar** bond or **co-ionic bond.** Some illustrations are given below :

(*i*) **Combination of Ammonia and Boron trifluoride** : In case of ammonia, nitrogen has five valence electrons. Out of these, three electrons are shared by three hydrogen atoms to form ammonia molecule while the remaining two electrons form a lone pair, which can be donated to any electron-deficient atom or molecule. In BF_3 molecule, boron is short of two electrons. So to complete its octet, it shares the lone pair of nitrogen, forming a dative bond as shown in Fig. 6.43.

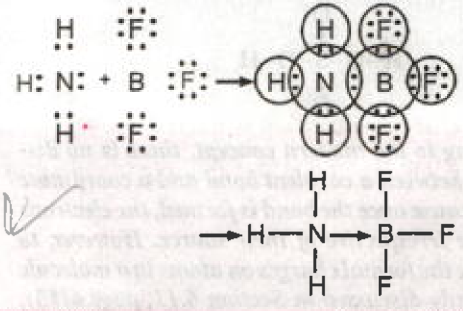


FIGURE 6.43. Formation of a co-ordinate bond between NH_3 and BF_3.

***(ii)* Sulphur Dioxide :** Sulphur as well as oxygen atoms have six valence electrons and each is short of two electrrons to complete its octet. In order to complete their octets, sulphur atom and oxygen atom, share two electrons each thus forming a double bond between them. Sulphur atom still has four unshared electrons, *i.e.*, two lone pairs to donate. Thus sulphur donates one lone pair to one oxygen atom, forming a co-ordinate bond between sulphur and oxygen and a molecule of sulphur dioxide. By accepting this lone pair, octet of oxygen is also completed, as represented in Fig. 6.44.

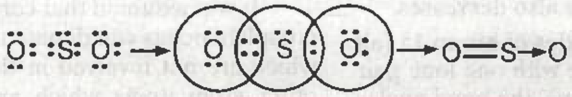


FIGURE 6.44. Formation of sulphur dioxide molecule.

***(iii)* Ammonium ion :** In NH_3, N atom has one lone pair of electrons. It can donate this lone pair to H^+ ion thus forming a co-ordinate bond as represented in Fig. 6.45.

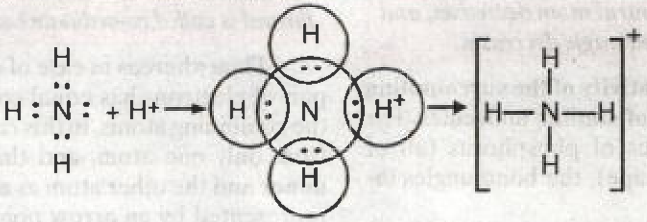
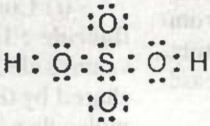
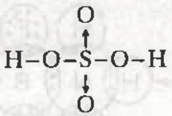


FIGURE 6.45. Formation of ammonium (NH_4^+) ion.

***(iv)* Sulphuric acid :** The Lewis structure of H_2SO_4 is as follows :



Evidently, S atom has two lone pairs of electrons which it can donate to two O-atoms forming co-ordinate bonds. Representing co-ordintae bonds by arrows, the above structure may be drawn as under :



$$\mathrm{H{-}O{-}\underset{\downarrow}{\overset{\uparrow}{S}}{-}O{-}H}$$ with O above and O below S.

According to the modern concept, there is no distinction between a covalent bond and a coordinate bond because once the bond is formed, the electrons are alike irrespective of their source. However, to calculate the formal charges on atoms in a molecule (as already discussed in Section 6.11, page 6/13), a distinction is made.

Co-ordinate bond in terms of Valence Bond Approach (Orbital concept).

A co-ordinate bond is formed by the overlap of a fully filled orbital containing a lone pair of electrons with the empty orbital of another atom.

This may be explained with the following examples :

***(i)* Formation of ammonium (NH_4^+) ion.** As already explained under the shape of NH_3 molecule, N atom in NH_3 still contains one hybrid orbital containing a lone pair of electrons. This orbital overlaps with the empty *s*-orbital of H^+ ion, forming a co-ordinate bond as shown in Fig. 6.46.

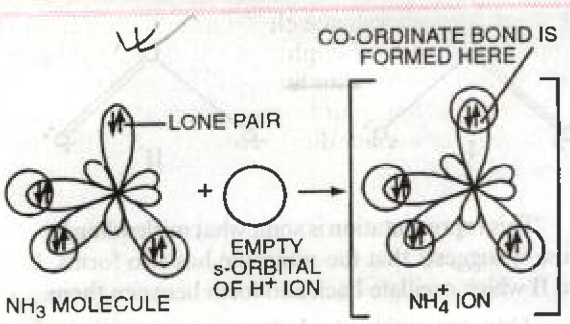


FIGURE 6.46. Formation of NH_4^+ ion (orbital concept).

(ii) Formation of hydronium (H_3O^+) ion. As already explained under the shape of H_2O molecule, the O-atom in H_2O still contains two sp^3 hybrid orbitals, each containing a lone pair of electrons. One of these orbitals overlaps with the empty orbital of H^+ ion, forming a co-ordinate bond as shown in Fig. 6.47.

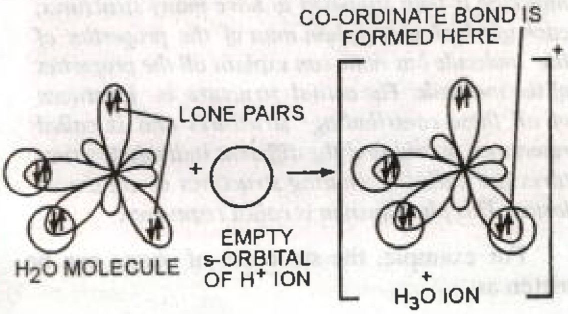
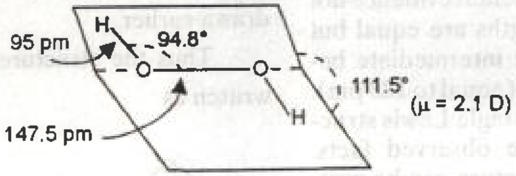


FIGURE 6.47. Formation of H_3O^+ ion (orbital concept).

ADD TO YOUR KNOWLEDGE

1. The dipole moment of CO molecule is greater than expected. This is because of the presence of a dative (co-ordinate) bond.
2. H_2O_2 molecule is said to have an open- book type structure as shown in the Fig. below :



3. The ability of the hybrid orbitals to overlap is in the order $sp^3 > sp^2 > sp$ *i.e.* greater is the *p*- character, greater is the ability to overlap.
4. The bond angles formed by different hybrid orbitals are in the order sp (180°) > sp^2 (120°) > sp^3 (109·5°) *i.e.* greater the *s*-character, greater is the bond angle.
5. The π-bond formed between S and O atoms in SO_2 molecule is due to overlap between their *p*-orbitals or between *p* orbital of O-atom with *d*-orbital of S- atom (called $p\pi - d\pi$ bonding)

$${}_{16}S = 1s^2\,2s^2\,2p^6\,3s^2\,3p_x^2\,3p_y^1\,3p_z^1$$

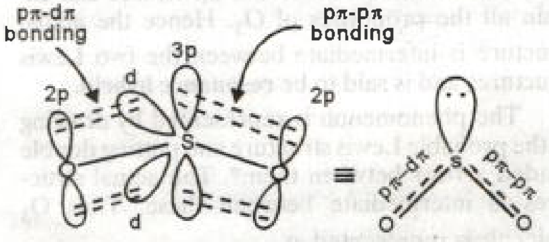
(Ground state configuration)

$$= 1s^2\,2s^2\,2p^6\,3s^1\,3p_x^1\,3p_y^1\,3p_z^1\,3d^1$$

(Excited state configuration)

$${}_{8}O = 1s^2\,2s^2\,2p_x^2\,2p_y^1\,2p_z^1$$

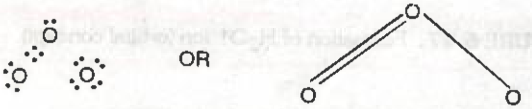
S-atom undergoes sp^2 hybridisation leaving one half-filled $3\,p_z$ orbital and one *d*-orbital unhybridized. Out of two half-filled orbitals of O-atom, one is involved in formation of σ-bond with S-atom and the other in forming π-bond as shown in the adjoining Fig.



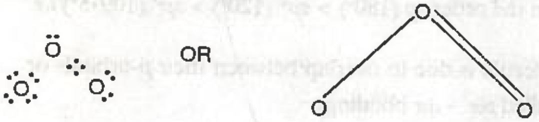
6.27. Resonance

In case of certain molecules, a single Lewis structure cannot explain all the properties of the molecule. The molecule is then supposed to have many structures, each of which can explain most of the properties of the molecule but none can explain all the properties of the molecule. The actual structure is inbetween of all these contributing structures and is called resonance hybrid and the different individual structures are called resonating structures or canonical forms. This phenomenon is called resonance.

For example, the structure of ozone can be written as

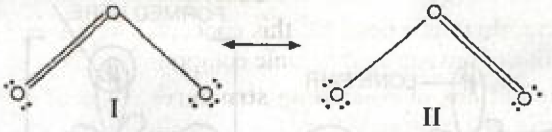


where each oxygen atom has an octet of electrons. But this structure is unsatisfactory because it depicts the central O atom to be bonded to one O atom by a double bond and the other O atom by a single bond. Since double bond is shorter than single bond, the two bond lengths in this molecule should be unequal (O – O single bond length = 148 pm, O = O double bond length = 121 pm). But experimental evidence not only shows that the bond lengths are equal but also shows that the bonds are intermediate between single and double bonds (equal to 128 pm). Hence for molecule like O_3, a single Lewis structure is unable to explain the observed facts. Hence an alternate Lewis structure can be written in which the double and single bonds are interchanged.



Neither of the above two structures can explain all the properties of O_3. Hence the actual structure is intermediate between the two Lewis structures and is said to be **resonance hybrid.**

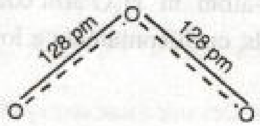
The phenomenon is represented by drawing all the probable Lewis structure and putting double headed arrows between them*. The actual structures is intermediate between these. Thus O_3 molecule is represented as



This representation is somewhat misleading because it suggests that the molecule has two forms, I and II which oscillate back and forth between them.

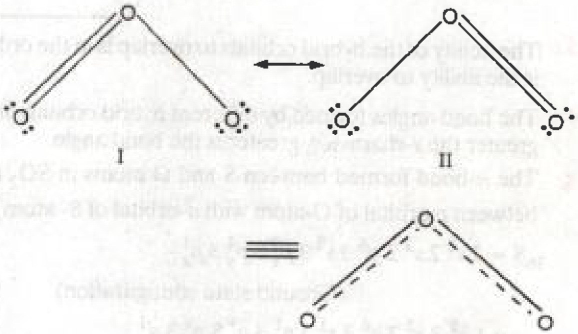
One can arrive at a better representation of the hybrid structure by superimposing one structure upon the other.

The result of this superimposition is shown below :



This representation indicates that (*i*) there is one stable hybrid form, (*ii*) this form is symmetrical, (*iii*) the two O – O bonds are of the same length (inbetween single bond and double bond) and (*iv*) the hybrid has an electronic arrangement intermediate between the two resonating structures drawn earlier.

Thus the structure of O_3 molecule may be written as



The resonance structures are arbitrary and imaginary and have no physical reality since neither of the two ozone structures, can be prepared in the laboratory.

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*The designation $\longleftrightarrow$ must be carefully distinguished from the designation $\rightleftharpoons$ which indicates reversible chemical reaction. The double headed arrow does not have any dynamic significance ; it merely implies that the molecule or ion is better represented by both structures than by one of them alone.

Since there are many molecules like O_3 whose behaviour cannot be explained by a single Lewis structure, there is a need for this concept. The resonance concept finds extensive use in explaining the behaviour of unsaturated organic compounds.

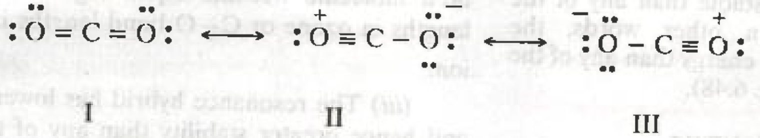
Conditions of resonating structures : It is of interest here to note that the different resonating structures of a substance have

(i) same positions of atoms (ii) same number of shared and unshared electrons (iii) almost equal energy.

They differ only in the arrangement of electrons in different resonating forms.

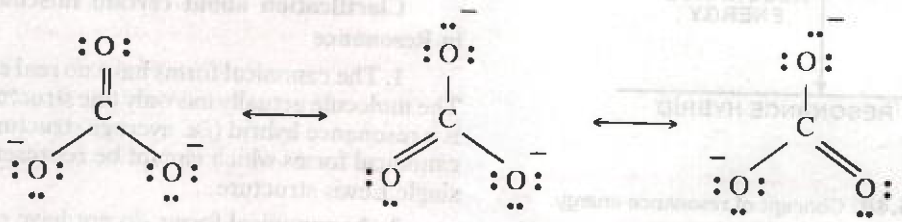
Examples of resonance structures of some more molecules and ions are given below :

(*i*) Carbon Dioxide (CO_2)*

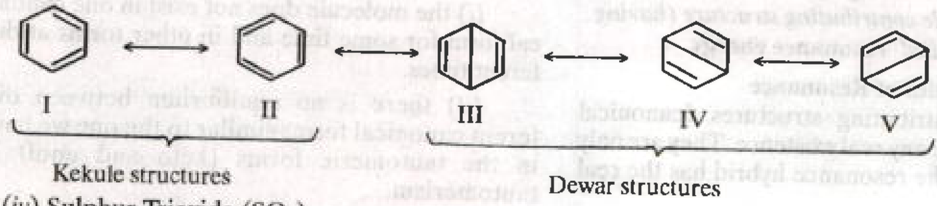


That the actual structure of CO_2 is a resonance hybrid of the above three structures is again supported by the fact that the experimentally determined value of both the bond lengths is same (*i.e.* 115 pm) which is inbetween that of C = O double bond (121 pm) and C ≡ O triple bond (110 pm).

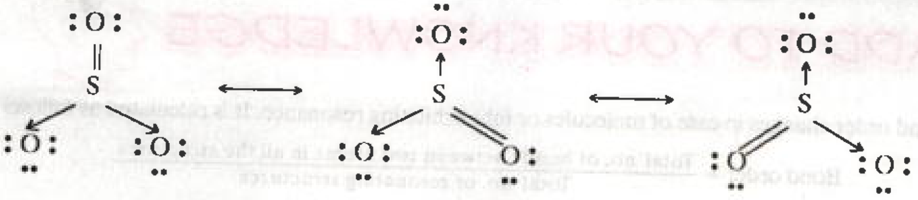
(*ii*) Carbonate Ion (CO_3^{2-})



(*iii*) Benzene (C_6H_6)**



(*iv*) Sulphur Trioxide (SO_3)



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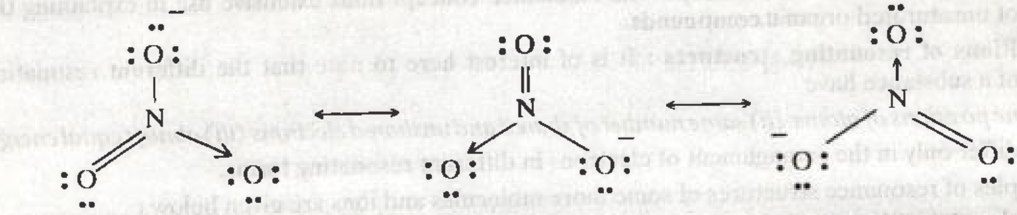
*For calculation of formal charge on each atom, see Sec 6.11 page 6/13.

**Structures III to V put forward by Dewar have one long bond and hence are less stable i.e. have higher energy. Hence the main contributing structures are I and II (put forward by Kekule).

(v) Nitrate Ion (NO_3^-)



Resonance energy. It may be noted that the resonance hybrid is more stable than any of the contributing structures. In other words, the resonance hybrid has lower energy than any of the contributing structures (Fig. 6.48).

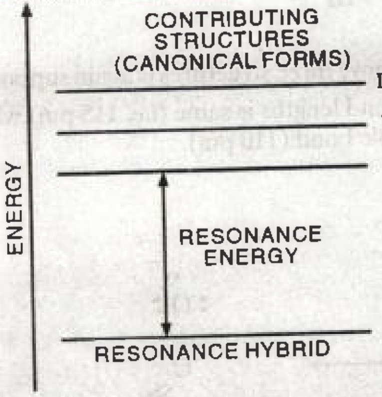


FIGURE 6.48. Concept of resonance energy.

***The difference in the energy of the resonance hybrid and the most stable contributing structure (having least energy) is called* resonance energy.**

Characteristics of Resonance

(i) The contributing structures (canonical forms) do not have any real existence. They are only imaginary. Only the resonance hybrid has the real existence.

(ii) As a result of resonance, the bond lengths in a molecule become equal e.g. O – O bond lengths in ozone or C – O bond lengths in CO_3^{2-} ion.

(iii) The resonance hybrid has lower energy and hence greater stability than any of the contributing structures.

(iv) Greater is the resonance energy, greater is the stability of the molecule.

(v) Greater is the number of canonical forms especially with nearly same energy, greater is the stability of the molecule.

Clarification about certain misconceptions in Resonance

1. The canonical forms have no real existence. The molecule actually nas only one structure which is a resonance hybrid (*i.e.* average structure) of the canonical forms which cannot be represented by a single Lewis structure.

2. As canonical forms do not have real existence, it should be clear in mind that

(i) the molecule does not exist in one canonical form for some time and in other forms at different times.

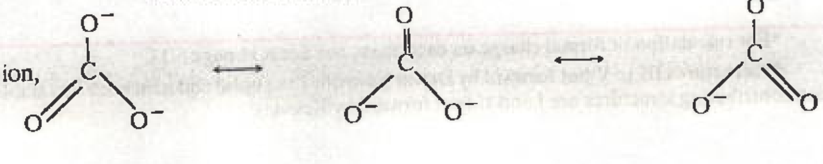
(ii) there is no equilibrium between different canonical forms similar to the one we have in the tautomeric forms (keto and enol) in tautomerism.

ADD TO YOUR KNOWLEDGE

1. The bond order changes in case of molecules or ions exhibiting resonance. It is calculated as follows :

$$\text{Bond order} = \frac{\text{Total no. of bonds between two atoms in all the structures}}{\text{Total no. of resonating structures}}$$

e.g. (i) In case of carbonate ion,

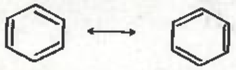


ADD TO YOUR KNOWLEDGE CONTD.

Looking at bonds of C-atom with a particular oxygen atom (say the one linked on the left) the bonds are 2, 1 and 1 respectively in the three structures and number of resonating structures is 3,

$$\therefore \quad \text{Bond order} = \frac{2+1+1}{3} = \frac{4}{3} = 1\cdot33$$

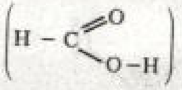
(*ii*) In case of benzene,



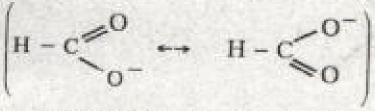
, Bond order $= \frac{1+2}{2} = 1\cdot5$

The observed value is, however, not exactly equal to 1·5 due to some other contributing structures.

2. In case of formic acid



, the two C—O bond lengths are different but in formate ion



the two C—O bond lengths are equal due to resonance.

6.28. Hydrogen Bonding*

1. Definition. Whenever a molecule contains a hydrogen atom linked to a highly electronegative atom (like F, O or N), this atom attracts the shared pair of electrons more and so this end of the molecule becomes slightly negative while the other end (*i.e.* H-end) becomes slightly positive. The negative end of one molecule attracts the positive end of the other and as a result, a weak bond is formed between them. This bond is called hydrogen bond. It is represented by dotted lines as shown below :

$$\overset{+\delta}{\mathrm{H}}-\overset{-\delta}{\mathrm{X}} \text{ ----- } \overset{+\delta}{\mathrm{H}}-\overset{-\delta}{\mathrm{X}} \text{ ------ } \overset{+\delta}{\mathrm{H}}-\overset{-\delta}{\mathrm{X}}$$

Thus, as a result of hydrogen bonding, a H-atom links the two electronegative atoms simultaneously, one by a covalent bond and the other by a hydrogen bond. Hence, it is said to form a **hydrogen bridge**.

2. Conditions for hydrogen bonding : In the formation of hydrogen bond, the following conditions must be fulfilled :

(*i*) *The molecule must contain a highly electronegative atom linked to H-atom.* The higher the electronegativity, more is the polarization of the molecule.

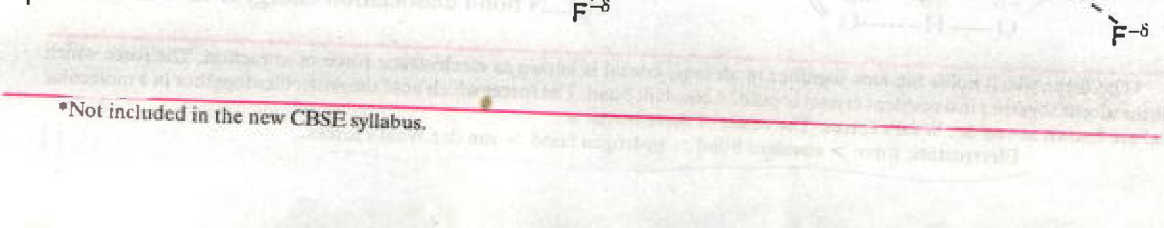
(*ii*) *The size of the electronegative atom should be small.* The smaller the size, the greater is the electrostatic attraction.

Thus, only F, O and N atoms can form hydrogen bonds, as these atoms are small in size and have high electronegativities.

Chlorine having the same electronegativity as that of nitrogen does not form hydrogen bond due to its large size.

3. Examples of hydrogen bonding :

(*i*) *Hydrogen fluoride* (HF) : Fluorine, having the highest value of electronegativity forms the strongest hydrogen bonds. Hydrogen fluoride, for example, exists as shown below :



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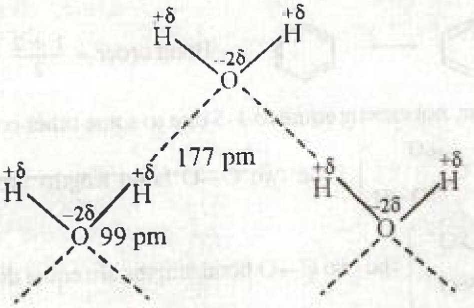
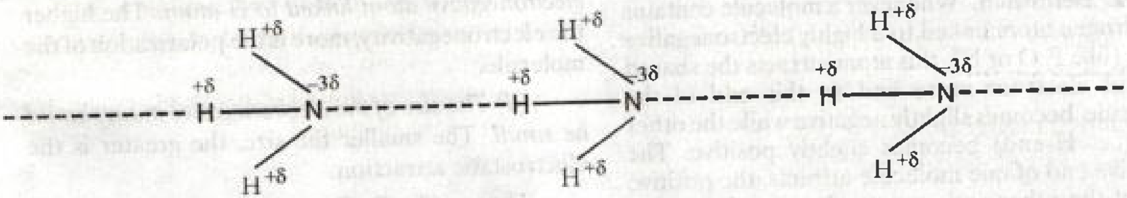
*Not included in the new CBSE syllabus.

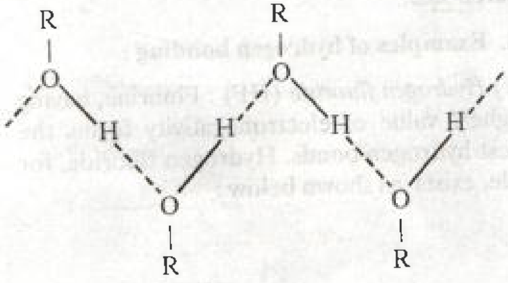
(*ii*) *Water* (H_2O) : Water molecule contains highly electronegative oxygen atom linked to hydrogen atom. Thus oxygen atom attracts the shared pair of electrons more and this end of the molecule becomes negative whereas the H-atom becomes positive. The negative end of one molecule attracts the positive end of the other and hydrogen bonding takes place as shown below :



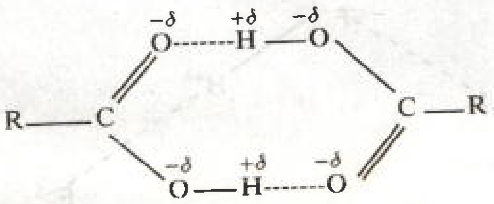
(*iii*) *Ammonia* (NH_3) : It contains the highly electronegative atom N linked to H-atoms. Hence, hydrogen bonding takes place as follows :



(*iv*) *Alcohols (ROH) and Carboxylic acids* (RCOOH) : These molecules contain the highly electronegative oxygen atom linked to H-atom and hence form associated molecules as follows :



ALCOHOLS



In case of HF, H_2O, NH_3, ROH etc., the hydrogen bonding causes the association of many molecules but in carboxylic acids, the hydrogen bonding is limited to the association of two molecules only.

4. Strength of hydrogen bond : Hydrogen bond is a very weak bond. The strength of hydrogen bond is intermediate between the weak van der Waal's forces and the strong covalent bonds*. Thus, whereas the bond dissociation energy of a covalent bond is 209 – 418 kJ mol^{-1}, that for H-bond is only 12·6 – 41·8 kJ mol^{-1}. The dissociation energy of the H-bond depends upon the attraction of the shared pair of electrons and hence on the electronegativity of the atom. The bond energies in case of three elements are as follows :

H......F bond dissociation energy is 41·8 kJ mol^{-1}.

H......O bond dissociation energy is 29·3 kJ mol^{-1}

H......N bond dissociation energy is 12·6 kJ mol^{-1}

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*The force which holds the ions together in an ionic crystal is known as electrostatic force of attraction. The force which holds the atoms together in a covalent crystal is called a covalent bond. The forces which hold the molecules together in a molecular crystal are known as van der Waal's forces. The order of these forces is

Electrostatic force > covalent bond > hydrogen bond > van der Waal's forces.

5. Difference between Hydrogen bond and Covalent bond. The main points of difference are given below :

HYDROGEN BOND	COVALENT BOND
(*i*) It involves dipole-dipole attractive interactions.	(*i*) It involves sharing of electrons.
(*ii*) It is formed between a hydrogen atom and a highly electronegative atom such as F, O and N.	(*ii*) It is formed between two electronegative atoms which may be of the same element or of different elements.
(*iii*) The strength of this bond is very small. *e.g.* bond strength of H.........F bond is 41·8 kJ mol^{-1}.	(*iii*) The bond strength of this bond is sufficiently high *e.g.*, bond strength of H—H bond is 433 kJ mol^{-1}.

6. Effects or Consequences of hydrogen bonding : Hydrogen bond helps in explaining the abnormal physical properties in serveral cases. Some of the properties affected by H-bond are given below :

(*i*) **Dissociation :** In aqueous solution, hydrogen fluoride dissociates and gives the difluoride ion (HF_2^-) instead of fluoride ion (F^-). This is due to H-bonding in HF. This explains the existence of KHF_2. On the other hand, the molecules of HCl, HBr, HI do not have H-bonding (because Cl, Br, I are not so highly electronegative). This explains the non-existence of compounds like $KHCl_2$, $KHBr_2$ or KHI_2.

(*ii*) **Association :** As mentioned in the examples above, the molecules of carboxylic acids exist as dimers because of the hydrogen bonding. The molecular masses of such compounds are found to be double than those calculated from their simple formulae. For example, molecular mass of acetic acid is found to be 120.

(*iii*) **High Melting and Boiling points :** The compounds having hydrogen bonding show abnormally high melting and boiling points. This is represented graphically in Fig. 6.49 for the elements of groups 14, 15, 16 and 17.

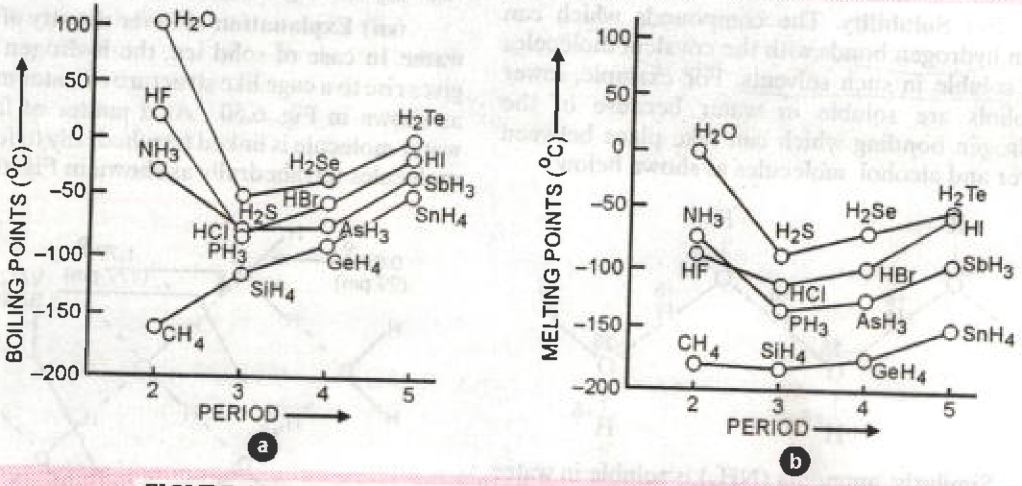

FIGURE 6.49. The abnormally high m.p. and b.p. of H_2O, NH_3 and HF.*

The high melting points and boiling points of the compounds (H_2O, HF and NH_3) containing hydrogen bonds is due to the fact that some extra energy is needed to break these bonds. A few examples are given below :

(*a*) *The unusually high boiling point of HF (292·4K) among the halogen acids* is due to the existence of hydrogen bonding in HF.

(*b*) *H_2O is a liquid whereas H_2S, H_2Se and H_2Te are all gases at ordinary temperature.* The

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***Note carefully** that boiling point of HI is less than that of HF but melting point of HI is greater than that of HF.

reason for this is that in case of water, hydrogen bonding causes association of the H_2O molecules with the result that the boiling point of water is more than that of the other compounds. On the other hand, there is no such hydrogen bonding in H_2S, H_2Se and H_2Te.

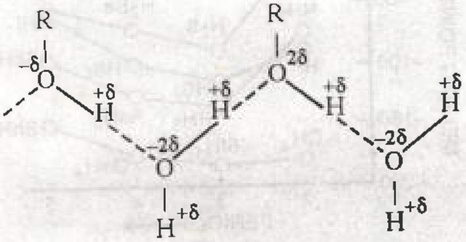
(*c*) *NH_3 has higher boiling point than PH_3.* This is again because there is hydrogen bonding in NH_3 but not in PH_3.

(*d*) *Ethanol has higher boiling point than diethyl ether* because there is hydrogen bonding in the former but there is no hydrogen bonding in the latter.

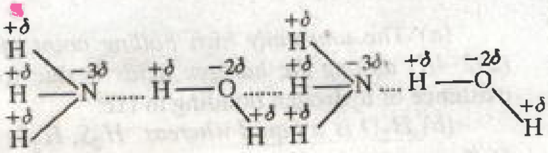
It is interesting to note that a stronger H-bond exists in HF than in H_2O, yet water boils at higher temperature than HF. It is probably due to the fact that water forms two H-bonds as compared to one in HF.

Further, it may be noted that the after the first significant decrease, the melting/boiling points of the subsequent members increase gradually. This is because as the size of the molecule increases, the van der Waals forces also increase.

(*iv*) Solubility. The compounds which can form hydrogen bonds with the covalent molecules are soluble in such solvents. For example, lower alcohols are soluble in water because of the hydrogen bonding which can take place between water and alcohol molecules as shown below :



Similarly, ammonia (NH_3) is soluble in water because of hydrogen bonding as represented below :



(*v*) Volatility. As the compounds involving hydrogen bonding between different molecules (intermolecular hydrogen bonding) have higher boiling points, so they are less volatile. The enthalpies of vaporisation follow almost the same trend as shown by the boiling points (Fig. 6.49(c)).

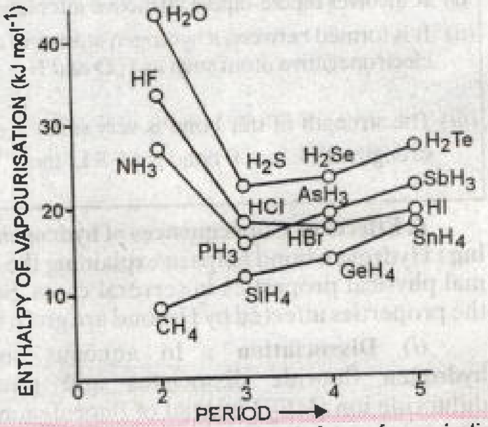


FIGURE 6.49(c). Variation of enthalpies of vaporisation (ΔH_{vap}) of the hydrides of elements of periods 2 to 5.

(*vi*) Viscosity and surface tension. The substances which contain hydrogen bonding exist as associated molecules. So their flow becomes comparatively difficult. In other words, they have higher viscosity and high surface tension.

(*vii*) Explanation of lower density of ice than water. In case of solid ice, the hydrogen bonding gives rise to a cage like structure of water molecules as shown in Fig. 6.50. As a matter of fact, each water molecule is linked tetrahedrally to four water molecules tetrahedrally as shown in Fig. 6.51.

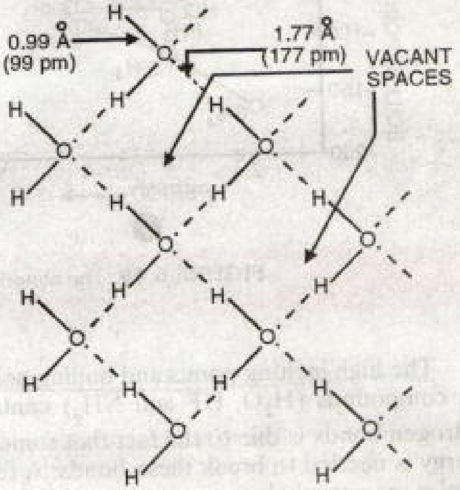


FIGURE 6.50. Cage like structure of H_2O in the ice.

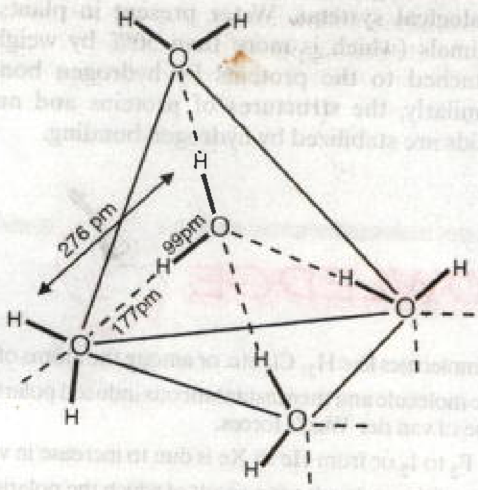


FIGURE 6.51. Each H_2O molecule linked to four H_2O molecules tetrahedrally.

Obviously, the molecules are not so closely packed as they are in the liquid state. When ice melts, this cage like structure collapses and the molecules come closer to each other. Thus, for the same mass of water, the volume decreases and hence density increases. Therefore ice has lower density than water at 273 K. That is why ice floats on water.

Note that each oxygen atom is linked to four H-atoms, two by covalent bonds and two by H-bonds. Each water molecule is linked to four water molecules tetrahedrally by H-bonds.

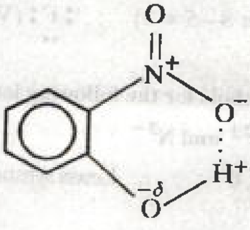
(*viii*) Explanation of maximum density of water at 277 K. At 273 K, there is sufficient hydrogen bonding present in the water molecules (or ice). Thus, the open cage-like structure exists which has larger volume and thus makes the density low. On heating, the hydrogen bonds start collapsing and thus the molecules start coming together resulting in the decrease of volume and hence increase of density. This goes on upto 277 K. After 277 K, the increase in volume due to expansion of the liquid water becomes much more than the decrease in volume due to breaking of H-bonds. Thus, after 277 K, there is net increase of volume on heating which means decrease in density. Hence density of water is maximum 277 K.

Thus the importance of hydrogen bond lies in the fact that it can explain the various abnormal physical properties.

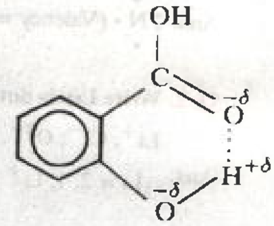
7. Types of Hydrogen bonding : There are two types of hydrogen bonding :

(*i*) Intermolecular hydrogen bonding : When hydrogen bonding takes place between different molecules of the same or different compounds, it is called intermolecular hydrogen bonding *e.g.*, HF, H_2O, ROH (same compound) and, water and alcohol or ammonia and water (different compounds) etc.

(*ii*) Intramolecular hydrogen bonding : The hydrogen bonding which takes place within a molecule itself is called intramolecular hydrogen bonding (or chelation). It takes place in compounds containing two groups such that one group contains a H- atom linked to an electronegative atom and other group contains a highly electronegative atom linked to a lesser electronegative atom. The bond is formed between the H-atom of one group with the more electronegative atom of the other group. A few examples involving intramolecular hydrogen bonding are given below :



o-Nitrophenol



Salicylic acid

Conditions of intramolecular hydrogen bonding. The following conditions must be satisfied for intramolecular hydrogen bonding :

(*i*) The molecule should contain two groups such that one group contains H-atom linked to a highly electronegative atom and the other group should also contain a highly electronegative atom linked to a lesser electronegative atom.

(*ii*) The molecule should be planar.

(*iii*) The hydrogen bonding should lead to the formation of a six membered ring including the H atom.

Effects of intramolecular hydrogen bonding. The intramolecular hydrogen bonding prevents association of molecules, causes a contraction of size of the molecules and hence decreases its surface area. Consequently, the effect of intramolecular hydrogen bonding on physical properties of substances is to lower their melting and boiling points, decrease their solubility and increase their vapour pressure, just opposite to what happens as a result of intermolecular hydrogen bonding.

8. Significance of hydrogen bonding in biological systems. Water present in plants and animals (which is more than 50% by weight) is attached to the proteins by hydrogen bonding. Similarly, the structures of proteins and nucleic acids are stabilized by hydrogen bonding.

ADD TO YOUR KNOWLEDGE

1. The forces of attraction that exist among the non-polar molecules like H_2, Cl_2 etc. or among the atoms of noble gases which are due to instantaneous polarisation of one molecule and then instantaneous induced polarization in the other are called **London forces.** These are a type of van der Waal's forces.
2. The increase in melting points and boiling points from F_2 to I_2 or from He to Xe is due to increase in van der Waal's forces which is turn are due to increase in the size of the molecules as a result of which the polarisability of the molecules becomes easier.

Conceptual Questions

Q. 1. Write the Lewis dot symbols and predict the valencies you expect for the following elements : Nitrogen, Fluorine and Neon

Ans. $:\overset{\cdot}{\underset{\cdot}{N}}\cdot$ (Valency = 5 or 8—5 = 3) ; $:\overset{\cdot}{\underset{\cdot\cdot}{F}}:$ (Valency = 7 or 8—7 = 1) ; $:\overset{\cdot\cdot}{\underset{\cdot\cdot}{Ne}}:$ (Valency = 0)

Q. 2. Write Lewis dot symbols for the following ions : (N.C.E.R.T.)

Li^+, Cl^-, O^{2-}, Mg^{2+} and N^{3-}

Ans. ${}_3Li$ = 2, 1, Li^+ = 2, 0 ∴ Lewis symbol = Li^+

${}_{17}Cl$ = 2, 8, 7, Cl^- = 2, 8, 8 ∴ Lewis symbol = $:\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}:^-$

${}_8O$ = 2, 6, O^{2-} = 2, 8 ∴ Lewis symbol = $:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:^{2-}$

${}_{12}Mg$ = 2, 8, 2, Mg^{2+} = 2, 8 ∴ Lewis symbol = Mg^{2+}

${}_7N$ = 2, 5, N^{3-} = 2, 8 ∴ Lewis symbol = $:\overset{\cdot\cdot}{\underset{\cdot\cdot}{N}}:^{3-}$

Q. 3. Is CaF_2 linear or bent or neither of the two ? Justify.

Ans. CaF_2 is neither linear nor bent molecule because it is ionic compound and ionic bond is non-directional.

Q. 4. What is co-ordination number of Na^+ and Cl^- ions in NaCl ?

Ans. Each has a co-ordination number of 6 *i.e.* each ion is surrounded by six oppsitely charged ions.

Q. 5. Out of NaCl and MgO, which has higher lattice energy and why ?

Ans. MgO has higher lattice energy because each ion carries two unit charge whereas in NaCl each ion carries one unit charge.

Q. 6. Why second electron affinity of an element is negative or second electron gain enthalpy is positive ?

Ans. After the addition of the first electron, we get a negative ion which has, therefore, a negative tendency to gain another electron *i.e.* energy is required for adding the second electron.

Q. 7. Why NaCl is a bad conductor of electricity in the solid state ?

Ans. In the solid state, Na^+ and Cl^- ions are not free.

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

Ans. NaCl is an ionic compound and hence gives Cl^- ions in the solution which combine with Ag^+ ions given by $AgNO_3$ to form a white precipitate of AgCl but CCl_4 is a covalent compound and does not give Cl^- ions.

Q. 9. Why reaction between NaCl and $AgNO_3$ is very fast but reaction between H_2 and Cl_2 is slow ?

Ans. NaCl and $AgNO_3$ are ionic compounds. In solution, NaCl gives Na^+ and Cl^- ions and $AgNO_3$ gives Ag^+ and NO_3^- ions. The oppositely charged Ag^+ and Cl^- ions combine immediately. The reaction between H_2 and Cl_2 involves breaking of covalent bonds which requires energy.

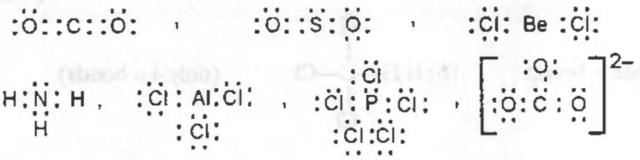
Q. 10. Define lattice enthalpy. How is it related to the stability of an ionic compound. *(N.C.E.R.T.)*

Ans. Definition see page 6/5. Greater the lattice enthalpy of an ionic compound, greater is the stability.

Q. 11. Draw the Lewis structures of the following molecules and ions and ions and tell in which case/cases the octet rule is violated

$$CO_2\ ,\ SO_2\ ,\ BeCl_2\ ,\ NH_3\ ,\ AlCl_3\ ,\ PCl_5\ ,\ CO_3^{2-}$$

Ans.



The octet rule is violated in case of $BeCl_2$, $AlCl_3$ and PCl_5.

Q. 12. Why two hydrogen atoms combine to form H_2 but two helium atoms do not combine to form He_2 ?

Ans. Refer to the text (on the basis of (*i*) New forces of attraction and repulsion and (*ii*) orbital concept).

Q. 13. Why free rotation about a π-bond is not possible?

Ans. The overlapping vanishes and the bond breaks.

Q. 14. Out of σ and π-bonds, which one is stronger and why ?

Ans. σ-bond is stronger. This is because σ-bond is formed by head-on overlapping of atomic orbitals and therefore the overlapping is large. π-bond is formed by sideway overlapping which is small.

Q. 15. What order of C—H bond lengths do you expect in C_2H_6 , C_2H_4 and C_2H_2 and why ?

Ans. C—H (C_2H_6) > C—H (C_2H_4) > C—H (C_2H_2). This is because hybrid orbitals of carbon involved in overlapping with 1*s* orbital of hydrogen are sp^3, sp^2 and sp respectively and their sizes are in the order $sp^3 > sp^2 > sp$.

Q. 16. Arrange the following in order of decreasing bond angles

(*i*) CH_4, NH_3, H_2O, BF_3, C_2H_2 (*ii*) NH_3, NH_2^-, NH_4^+

Ans. (*i*) $C_2H_2(180°) > CH_4\ (109° 28') > BF_3\ (120°) > NH_3\ (107°) > H_2O\ (104{\cdot}5°)$.

(*ii*) $NH_4^+ > NH_3 > NH_2^-$

This is because all of them involve sp^3 hybridization. The number of lone pair of electrons present on N-atom are 0, 1 and 2 respectively. Greater the number of lone pairs, greater are the repulsions on the bond pairs and hence smaller is the angle.

Q. 17. Which of the following molecule/molecules will have zero dipole moment ?
$CO_2, H_2O, CCl_4, CHCl_3, BF_3, BeF_2, NH_3$.

Ans. CO_2 , CCl_4 , BF_3 and BeF_2.

Q. 18. Which bond do you expect to be stronger in each of the following cases and why ?
***(i)* H — H, Cl—Cl, *(ii)* O_2 , N_2 *(iii)* F—F, Cl—Cl**

Ans. *(i)* H —H is stronger because of smaller size of H—atoms.

(ii) N ≡ N is stronger because it contains a triple bond while O_2 contains a double bond (O = O).

(iii) Cl—Cl is stronger because repulsions between the two F-atoms in F_2 are larger on account of greater electron density around F-atom due to smaller size and hence greater repulsions between the two F-atoms.

Q. 19. Define electronegativity. How does it differ from electron affinity ? *(N.C.E.R.T.)*

Ans. Definition—See page 6/23. Difference between EN and EA—See page 6/25.

Q. 20. 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.)*

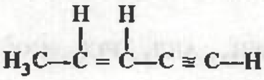
Ans. $N_2 < SO_2 < ClF_3 < K_2O <$ LiF

Q. 21. Arrange the following bonds in the order of increasing ionic character :
C—H, F—H, Br—H, Na—I, K—F and Li—Cl *(N.C.E.R.T.)*

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

Q. 22. What is the total number of sigma and pi bonds in the following molecules ?

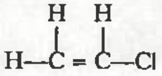
(a)* C_2H_3Cl *(b)* CH_2Cl_2 *(c)



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

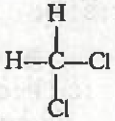
(N.C.E.R.T.)

Ans. *(a)* is



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

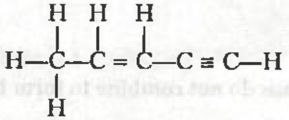
(5 σ bonds, one π bond) *(b)* is



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

(only 4 σ bonds)

(c) is



$H-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\overset{\overset{H}{|}}{C}=\overset{\overset{H}{|}}{C}-C\equiv C-H$

(10 σ bonds, 3 π bonds)

Q. 23. Taking *x*-axis as the internuclear axis, which out of the following will form σ-bond ?
(i)* 1 *s* and 1 *s* *(ii)* 1 *s* and $2p_x$ *(iii)* $2p_y$ and $2p_y$ *(iv)* 1 *s* and 2 *s*. *(N.C.E.R.T.)

Ans. All except *(iii)*.

Q. 24. What is meant by 'bond order' according to Lewis concept ? Calculate the bond order of N_2, O_2 and CO. *(N.C.E.R.T.)*

Ans. Bond order—Definition see page 6/23.

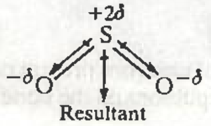
Molecule :	N ≡ N	O = O	C ≡ O
Bond order :	3	2	3

Q. 25. Explain why dipole moment of hydrogen halides decreases from HF to HI. *(N.C.E.R.T.)*

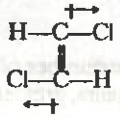
Ans. This is because electronegativity of halogen atom dcreases from F to I. Hence the polar character decreases and so is the dipole moment.

Q. 26. Represent diagramatically the bond moments and the resultant dipole moments in
(i)* SO_2 *(ii)* cis and trans forms of $C_2H_2Cl_2$ *(N.C.E.R.T.)

Ans. *(i)*



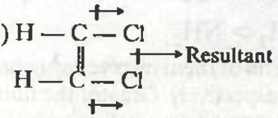
(ii)



trans−(μ = 0)

Resultant = 0

(iii)



cis−(μ ≠ 0)

Q. 27. **Predict which out of the following molecules will have higher dipole moment and why ?**

CS_2 and OCS *(N.C.E.R.T.)*

Ans. $\overset{\leftarrow\!+\quad +\!\rightarrow}{S = C = S}$ and $\overset{\leftarrow\!+\quad +\!\rightarrow}{O = C = S}$ both are linear molecules but bond moments in CS_2 cancel out so that net dipole moment = 0. 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. 28. **From each of the following pairs, select the molecule with higher value of the property mentioned against each pair :**

(*i*) NH_3, PH_3 : bond angle **(*ii*) NF_3, NH_3 : dipole moment**

(*iii*) MgO, CaO : hardness **(*iv*) HCl, HBr : ionic character**

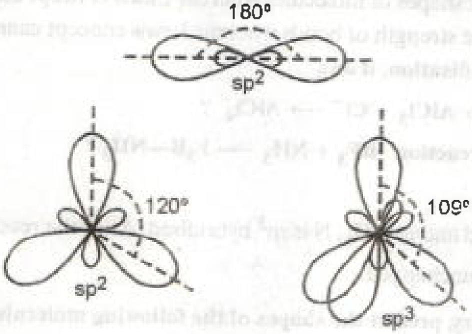
Ans. (*i*) NH_3 (*ii*) NH_3 (*iii*) MgO (*iv*) HCl

Q. 29. **Write the structure of an anion which is isostructural with BF_3 and the structure of a cation which is isostructural with CH_4**

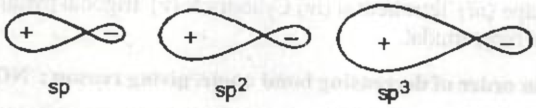
Ans. (*i*) NO_3^- (Triangular planar) (*ii*) NH_4^+ (tetrahedral)

Q. 30. **Draw the shapes of the following hybrid orbitals :** ***sp*, *sp*^{2} and *sp*^{3}** *(N.C.E.R.T.)*

Ans.



All the hybrid orbitals have same shape. However their sizes are in the order $sp < sp^2 < sp^3$



Q. 31. **Explain how the valence bond theory accounts for**

(*i*) a carbon-carbon double bond (C = C) (*i*) a carbon-carbon triple bond (C ≡ C) *(N.C.E.R.T.)*

Ans. Explain with examples of ethylene and acetylene (page 6/39 and 6/40).

Q. 32. **Explain why CH_4 has tetrahedral geometry and not square planar with carbon atom at the centre and four H atoms at the corners of the square.**

Ans. The hybridisation of central C-atom is sp^3 and not dsp^2 (as no *d*-orbital is available for participation). Hence square planar geometry is not possible.

Q. 33. **Name the type of hybridisation of each C-atom in a molecule of (*i*) propylene (propene) (*ii*) Propyne How many σ and π-bonds are present in each case?**

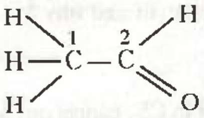
Ans. (*i*) $\overset{1}{C}H_3—\overset{2}{C}H = \overset{3}{C}H_2$ (C—1 is sp^3, C—2 and C—3 are sp^2), σ-bonds = 8, π-bonds = 1.

(*ii*) $\overset{1}{C}H_3—\overset{2}{C} \equiv \overset{3}{C}H$ (C—1 is sp^3, C—2 and C—3 are *sp*), σ-bonds = 6, π-bonds = 2.

Q. 34. **Which hybrid orbitals are used by carbon atoms in the following molecules ?**

(*i*) CH_3—CHO (*ii*) CH_3—COOH.

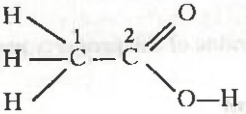
Ans. (*i*)



C—1 is sp^3 hybridised

C—2 is sp^2 hybridised

(*ii*)



C—1 is sp^3 hybridised

Q. 35. In SF_4 molecule, the lone pair of electrons occupies an equatorial position rather than axial position in the overall trigonal bipyramidal arrangement. Why ? *(N.C.E.R.T.)*

Ans. The *lp* – *bp* repulsions are less if it occupies equatorial position than if it occupies axial position. As a result, energy is less and stability is more (see page 6/44).

Q. 36. Explain how VB theory differs from Lewis concept.

Ans. (*i*) According to Lewis concept, a covalent bond is formed by mutual sharing of electrons whereas according to VB theory a covalent bond is formed by the overlap of half-filled atomic orbitals containing electrons with opposite spin.

(*ii*) VB theory can explain the shapes of molecules whereas Lewis concept cannot.

(*iii*) VB theory can explain the strength of bonds whereas Lewis concept cannot.

Q. 37. Describe the change in hybridisation, if any,

(*a*) of Al atom in the reaction $AlCl_3 + Cl^- \longrightarrow AlCl_4^-$?

(*b*) of B and N atoms in the reaction $BF_3 + NH_3 \longrightarrow F_3B—NH_3$? *(N.C.E.R.T.)*

Ans. (*a*) No change (remains sp^3)

(*b*) In BF_3, B is sp^2 hybridised and in NH_3, N is sp^3 hybridised. After the reaction, hybridisation of B changes to sp^3 but that of N remains unchanged.

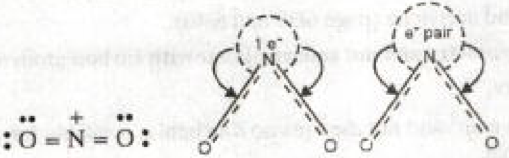
Q. 38. On the basis of VSEPR theory, predict the shapes of the following molecules/ions ?

(*i*) SiF_4 (*ii*) NH_2^- (*iii*) NH_4^+ (*iv*) C_2H_2 (*v*) H_3O^+ (*vi*) F_2O (*vii*) PCl_3 (*viii*) PF_5.

Ans. (*i*) Tetrahedral (*ii*) V-shape (*iii*) Tetrahedral (*iv*) Cylindrical (*v*) Trigonal pyramidal (*vi*) V-shape (*vii*) Trigonal pyramidal (*viii*) Trigonal bipyramidal.

Q. 39. Arrange the following in order of decreasing bond angle, giving reason : NO_2, NO_2^+, NO_2^-

Ans. $NO_2^+ > NO_2 > NO_2^-$. This is because NO_2^+ has no unshared electron and hence it is linear. NO_2 has one unshared electron while NO_2^- has one unshared electron pair.



Bond angle = 180° Bond angle = 132° Bond angle = 115°

Q. 40. Why axial bonds of PCl_5 are longer than equatorial bonds ?

Ans. This is due to greater repulsion on the axial bond pairs by the equatorial bond pairs of electrons.

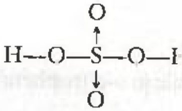
Q. 41. Why NF_3 is pyramidal but BF_3 is triangular planar?

Ans. In NF_3, N has the hybridisation sp^3 with one position occupied by lone pair of electrons but in BF_3, B has the hybridisation sp^2.

Q. 42. Why bond angle in H_2O is nearly 104·5° but that in H_2S, it is nearly 90° ?

Ans. Refer to the text (page 6/44).

Q. 43. **Draw the structure of H_2SO_4. What is hybridisation of S-atom in it ?**

Ans. 
$\mathrm{H—O—\underset{\downarrow \atop O}{\overset{O \atop \uparrow}{S}}—O—H}$. Hybridisation of S-atom is sp^3.

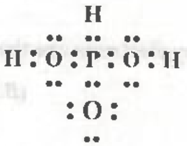
Q. 44. **Out of *p*-orbital and *sp*-hybrid orbital which has greater directional character and why ?**

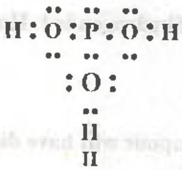
Ans. *sp*-orbital has greater directional character than *p*-orbital. This is because *p*-orbital has equal sized lobes with equal electron density in both the lobes wheres *sp*-hybrid orbital has greater electron density on one side.

Q. 45. **Explain the important aspects of resonance with reference to CO_3^{2-} ion.** *(N.C.E.R.T.)*

Ans. See resonating structures on page 6/49. All the three bonds are exactly identical in bond strength and bond length.

Q. 46. **H_3PO_3 can be represented by the structures I and II shown below. Can these two structures be taken as the canonical forms of the resonance hybrid of H_3PO_3. If not, state reason for the same**


I


II

(N.C.E.R.T.)

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

Q. 47. **Why H_2O is a liquid while H_2S is a gas ?**

Ans. In H_2O, there is hydrogen bonding and hence association of H_2O molecules but in H_2S there is no H-bonding.

Q. 48. **Why HF has higher boiling point than HCl ?**

Ans. In HF there is H-bonding and hence the molecules are associated together but in HCl there is no H-bonding.

Q. 49. **Why ethyl alcohol is completely miscible with water ?**

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

Q. 50. **Why KHF_2 exists but $KHCl_2$ does not ?**

Ans. Due to H-bonding in HF, we have H—F-----H—F-----H—F-----.

This can dissociate to give HF_2^- ion and hence KHF_2 exists but there is no H-bonding in H—Cl. So HCl_2^- ion does not exist and hence $KHCl_2$ also does not exist.

Q. 51. **When we move from HF to HCl, the boiling point drops sharply but on moving further to HBr and HI the boiling point increases. Why ? or Out of HF, HCl , HBr and HI which has lowest boiling point and why ?**

Ans. In H—F there is H-bonding. Hence the boiling point is high. There is no H-bonding in HCl. So the boiling point is less. On moving further to HBr and HI, the size of the molecule increases and so the van der Waal's forces increase and so does the boiling point. Hence HCl has the lowest boiling point.

Q. 52. **Ethanol has higher boiling point than diethyl ether or ethylamine. Why ?**

Ans. In ethanol, there is H-bonding but in diethyl ether, there is no H-bonding (because O-atom is attached to C-atom) and in case of ethylamine the H-bonds formed by N-atom are weaker than those formed by O-atom.

Q. 53. **Why ice has lower density than water or why ice floats on the surface of water ?**

Ans. See text (page 6/54).

Q. 54. **Why water has maximum density at 277 K ?**

Ans. Refer to the text (page 6/54).

Q. 55. **How many H-bonds are formed by each H_2O molecule and how many water molecules are attached to each water molecule and in what direction ?**

Ans. Each H_2O molecule forms four H-bonds, two with O-atom and two with H-atoms. Further, each H_2O molecule is linked to four H_2O molecules through H-bonds tetrahedrally.

Q. 56. Out of *o*-nitrophenol and *p*-nitrophenol which has higher boiling point and why ?

Ans. *p*-nitrophenol has higher boiling point because there is intermolecular H-bonding while in *o*-nitrophenol, there is intramolecular H-bonding.

Q. 57. Though Cl has nearly same electronegativity as N, yet there is no H-bonding in HCl. Why ?

Ans. Chlorine atom has a large size.

Q. 58. Why glucose, fructose, sucrose etc. are soluble in water though they are covalent compounds ?

Ans. These compounds contain polar —OH groups which can form H-bonds with water.

Q. 59. Benzene ring contains alternate single and double bonds, yet all the C—C bonds are of equal length. Why ?

Ans. This is due to resonance in benzene.

Q. 60. Nitrogen has an atomic number of 7 and oxygen has an atomic number of 8. The total number of electrons in nitrate ion (NO_3^-) is .... *(B.I.T. Ranchi 1990)*

Ans. Electrons in $NO_3^- = 7 + 3 \times 8 + 1 = 32$.

Q. 61. The atomic number of nitrogen is 7 and that of hydrogen is 1. How many electrons are there in ammonium ion, NH_4^+ ? *(B.I.T. Ranchi 1991)*

Ans. No. of electrons in $NH_4^+ = 7 + 4 - 1 = 10$.

Q. 62. Sodium metal vaporises on heating and the vapour will have diatomic molecules of sodium (Na_2). What type of bonding is present in these molecules ? *(B.I.T. Ranchi 1991)*

Ans. Covalent bonding.

Q. 63. Out of P—F, F—F, S—F and Cl—F bonds, which bond is the least ionic ? *(B.I.T. Ranchi 1992)*

Ans. F—F.

Q. 64. Why is water a liquid whereas H_2Se is a gas ? *(I.S.M. Dhanbad 1993)*

Ans. There is hydrogen bonding in H_2O but no hydrogen bonding in H_2Se.

Q. 65. Why an ionic bond is formed between two elements having large difference in their electronegativity ? *(Bihar 1997)*

Ans. The more electronegative element will attract the shared pair of electrons to such a large extent than the other that it will amount to transfer of electron resulting in the formation of ions.

Q. 66. Which of the following has maximum bond angle ?

H_2O, CO_2, NH_3, CH_4. *(Bihar 1997)*

Ans. CO_2, 180° (due to linear structure)

Q.67. What angles are associated with the following orbitals ?

***sp*, *sp*^{2} and *sp*^{3}** *(B.I.T. Ranchi 2000)*

Ans. $sp = 180°$, $sp^2 = 120°$, $sp^3 = 109°28'$.

Q. 68. Write down the Lewis structures of the following : (*i*) CO_2 (*ii*) CN^- *(Bihar C.E.E. 2003)*

Ans. Refer to sec. 6.10, page 6/10.

Very Short Answer Questions CARRYING 1 MARK

Q. 1. Which electrons take part in bond formation?

Ans. Valence electrons present in the outermost shell.

Q. 2. What change in energy takes place when a molecule is formed from its atoms ?

Ans. Lowering of energy takes place.

Q. 3. What type of forces hold the atoms together in an ionic compound ?

Ans. Electrostatic forces of attraction.

Q. 4. In terms of ionization energy and electron affinity, what type of atoms combine to form an ionic compound ?

Ans. Metal atom with low I.E. and a non-metal atom with high E.A.

Q. 5. Choose the compounds containing ionic, covalent and co-ordinate bonds out of the following :

$$MgCl_2, CH_4, CaO, HCl, NH_4^+, O_3$$

Ans. Ionic = $MgCl_2$, CaO ; covalent = CH_4, HCl ; co-ordinate = NH_4^+, O_3

Q. 6. What type of orbitals can overlap to form a covalent bond ?

Ans. Half-filled atomic orbitals containing electrons with opposite spin.

Q. 7. What orbitals can overlap to form a σ-bond and which orbitals can do so to form a π-bond ?

Ans. *s-s*, *s-p*, *p-p* for σ-bond and only *p-p* for π-bond.

Q. 8. Name one compound each involving sp^3 , sp^2 and *sp* hybridisation.

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

Q. 9. Name the shapes of the following molecules : CH_4 , C_2H_2 , CO_2

Ans. CH_4=tetrahedral, C_2H_2=cylindrical, CO_2=linear.

Q. 10. Name the two conditions which must be satisfied for hydrogen bonding to take place in a molecule.

Ans. (*i*) The molecule should contain a highly electronegative atom linked to H-atom.

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

Q. 11. In forming a compound XY, atoms of X lose one electron each while the atoms of Y acquire one electron each. Predict the nature of the compound.

Ans. The compound XY is ionic in nature.

Q. 12. Predict the dipole moment of a molecule of the type AX_4 with square planar arrangement of X atoms.

Ans. zero.

Q. 13. Identify the compound/compounds in the following in which S does not obey the octet rule.

$$SO_2 , SF_2 , SF_4 , SF_6$$

Ans. SF_4 , SF_6.

Q. 14. You are given the electronic configuration of five neutral atoms — A, B, C, D and E.

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 — $1s^2\ 2s^2\ 2p^6$ **E** — $1s^2\ 2s^2\ 2p^6$.

Write the empirical formula for the substance containing (*i*) A and D (*ii*) B and D (*iii*) only D (*iv*) only E ?

Ans. (*i*) Empirical formula of the compound formed by A and D is AD_2 as A has two valence electrons and D has seven. Atom A transfers its two electrons to two D atoms to complete their octets.

(*ii*) Empirical formula of the compound formed by B and D is BD as B transfers its one electron to D.

(*iii*) D_2 as both the atoms of D share one electron each to form a covalent bond.

(*iv*) Since it is a noble gas, no compound is formed.

Q. 15. Arrange the following in order of increasing bond strengths : F_2 , N_2 , O_2 , Cl_2 *(B.I.T. Ranchi 1992)*

Ans. $F_2 < Cl_2 < O_2 < N_2$.

Q. 16. Arrange the following in order of increasing strength of hydrogen bonding : O, F, S, Cl, N *(M.L.N.R. Allahabad 1993)*

Ans. Cl < S < N < O < F.

Q. 17. What is valence bond approach for the formation of covalent bond and a co-ordinate bond ?

Ans. A covalent bond is formed by the overlap of half filled atomic orbitals whereas a co-ordinate bond is formed by the overlap of an empty orbital with a fully-filled orbital.

Q. 18. Name the method generally used for the calculation of lattice energy or electron affinity.

Ans. Born-Haber cycle.

Q. 19. What are SI units of dipole moment ?

Ans. Coulomb meter (Cm).

Short Answer Questions CARRYING 2 or 3 MARKS

Sec. 6.1. to 6.8.

1. What do you understand by a chemical bond ?
2. Briefly explain Kossel-Lewis approach of chemical bonding.
3. Illustrate the inadequacy of octet rule with two suitable examples. Give the Lewis structure of these molecules.
4. Why are the noble gases poor chemical reactants?
5. What happens when two hydrogen atoms approach each other ?
6. On the basis of electronic theory, briefly explain the different modes of chemical combination between atoms.
7. Explain the term electrovalency.
8. Briefly explain the factors which influence the formation of the ionic compounds.
9. What are the important characteristics of ionic compounds ?
10. NaCl is a better conductor of electricity in a molten condition than in the solid state. Explain.
11. What is an electrovalent bond (or ionic bond) ? Explain its formation with two suitable examples.
12. An element A combines with element B. An atom of A contains two electrons in its outermost shell whereas that of B has six electrons in its outermost shell. Two electrons are transferred from the atom A to the atom B.
    (*a*) What is the nature of bond between A and B ?
    (*b*) What is the electronic structure of AB ?
    (*c*) What is the electrovalency of A and that of B ?
13. Name two conditions that are essential for two different atoms to form ionic bond.
14. Define Lattice energy. On what factors does it depend ? How does it help to predict the stability of the ionic compound formed ?
15. How can the electron affinity of chlorine be determined using Born-Haber cycle ? (*N.C.E.R.T.*)

Sec. 6.9. to 6.15.

16. What is meant by a covalent bond ? Explain with three suitable examples. What are the conditions for the formation of this type of bond ?
17. What are Lewis structures ? Write the Lewis structures of H_2, F_2, H_2O, NH_3, C_2H_4 and C_2H_2.
18. Explain the term covalency.
19. Briefly discuss the orbital concept of covalent bond formation taking suitable examples.
20. How is the formal charge on an atom in a molecule/ion calculated ? Explain taking the example of ozone molecule.
21. Differentiate between σ and π bonds.
22. Explain how the strength of a bond is related to (*i*) extent of overlapping (*ii*) shape of the orbital.
23. What are sigma and pi bonds ? Explain the different ways of their formation diagrammatically. Which one of them is stronger and why ?

Sec. 6.16.

24. Arrange the following according to bond length giving reasons :
    (*i*) H—F, H—Cl, H—Br, H—I
    (*ii*) C—C, C=C, C≡C
    (*iii*) C—H bond length in CH_4, C_2H_4 and C_2H_2
25. Arrange the following single bonds in order of bond energy giving reasons :
    C—C, N—N, O—O, F—F

Sec 6.17. to 6.20. **26.** Define the term Electronegativity. Explain it with one suitable example. How does it help in predicting whether a covalent bond is polar or non-polar ? Explain each case with one example.

27. Define 'Electronegativity'. How is it calculated on (*i*) Pauling scale (*ii*) Mulliken scale How are the two values related to each other ?

28. Which of the following hydrogen halides has the most polar molecules and why ?
HI, HBr, HCl, HF.

29. HF is more polar than HI. Explain why ?

30. What do you understand by partial ionic character of covalent bonds?

31. Define Dipole moment. Draw dipole diagrams of H_2O and BF_3.

32. Explain : Each carbon-oxygen bond in CO_2 molecule is polar but the molecule itself is non-polar.

33. Explain the term Dipole moment. Name two molecules which have a dipole moment and two molecules which do not have a dipole moment. What is the significance of dipole moment ?

34. Explain giving reasons, which of the following molecules have electric dipoles
(*a*) CCl_4 (*b*) $CHCl_3$ (*c*) CH_2Cl_2 (*d*) CH_3Cl (*e*) CH_4.

35. Give reason for the following :
(*i*) Ionic compounds are soluble in water whereas covalent compounds are mostly insoluble in water.
(*ii*) Ionic compounds have higher melting points than the covalent compounds.
(*iii*) NaCl solution gives a white ppt with $AgNO_3$ solution but CCl_4 or chloroform does not.

Sec 6.23. to 6.24. **36.** What are the main postulates of Valence Shell Electron Pair Repulsion (VSEPR) theory ? What improvement was made by Nyholm and Gillespie ?

37. What is hybridisation of orbitals ? Draw outline sketches to show the formation of *sp*, sp^2 and sp^3 hybrid orbitals.

38. What type of hybridisation is associated with the central atom when the atoms attached to it form (*a*) an equilateral triangle (*b*) a regular tetrahedron ?

39. Explain why carbon has a valency of four and not two and why are the four C-H bonds in methane identical.

40. Explain the term Hybridisation taking the example of methane.

41. Carbon has electronic configuration $1s^2\ 2s^2\ 2p^2$ and, therefore, should be bivalent. How will you justify its tetravalency in methane ?

42. Define hybridisation. Describe the formation of sp^3, sp^2 and sp hybrid orbitals of carbon atom. Give one example of a molecule in each case involving these different types of hybridisation.

43. What is valence bond approach of covalent bond ? Give two examples to illustrate it.

Sec. 6.25. **44.** Making use of the concept of hybridisation, predict the shape of C_2H_2 molecule.

45. Draw shapes of H_2O and C_2H_4.

46. Using the valency shell electron pair repulsion (VSEPR) model, predict the shapes of the following molecules (*i*) $BeCl_2$ (*ii*) BF_3.

47. Suggest the expected shape of NH_3.

48. Draw well labelled orbital diagrams for the following molecules
(*i*) BeF_2 (*ii*) BF_3 (*iii*) CH_4 (*iv*) NH_3 (*v*) C_2H_6.

49. Predict the shapes of the following molecules using the valence shell electron pair repulsion model.
(*i*) $BeCl_2$ (*ii*) SiF_4 (*iii*) BF_3 (*iv*) NH_3 (*v*) H_2O.

50. Explain the shapes of SF_4 and ClF_3.

Sec 6.26. **51.** What is a coordinate bond ? Explain with two suitable examples. How is it different from a covalent bond ?

Sec 6.27. **52.** What is resonance ? Define Resonance energy.

53. Draw the resonating structures of CO_2 ?

Sec 6.28. **54.** What is hydrogen bonding ? Give three examples of molecules involving hydrogen bonding. How is hydrogen bond different from an ionic bond and a covalent bond ?

55. Account for the following :

(*i*) Water is a liquid while H_2S is a gas. (*ii*) NH_3 has higher boiling point than PH_3.

(*iii*) Boiling point of HF is lower than that of water.

56. What is hydrogen bonding ? In what respects is it different from ionic and covalent bonding ?

57. Write a short note on 'Hydrogen bond'.

58. Explain why ordinarily H_2S is a gas while H_2O a liquid even though both S and O are elements of the same group in the periodic table and S has a higher atomic mass.

59. Water is a liquid and hydrogen sulphide is a gas, although the molecular mass of hydrogen sulphide is almost double that of water. Explain.

60. What requirement should a molecule fulfil for the formation of a hydrogen bond ?

61. Give one example of intramolecular hydrogen bond.

62. The boiling and melting points of water are abnormally higher than those of other hybrides of group 16 of the periodic table. Give reasons.

Long Answer Questions CARRYING 5 or more MARKS

Sec 6.1. to 6.8. **1.** What do you mean by a chemical bond ? How do atoms combine ? How many types of bonds are there ?

2. What are essential conditions for the formation of an ionic bond ? Explain the formation of an ionic bond between an atom of Na and Cl.

3. Describe various characteristics of electrovalent compounds.

4. How can the lattice enthalpy of an ionic compound like NaCl be determiend by using Born-Haber cycle ?

Sec. 6.9. to 6.15. **5.** Explain the formation of covalent bond on the basis of (*i*) Lewis concept (*ii*) Valence Bond theory, taking at least three suitable examples in each case.

6. Briefly describe Valence Bond Theory of covalent bond. How can you interpret it in terms of energy considerations ?

7. What are sigma and pi bonds ? Explain the different ways of their formation diagrammatically. Which one of them is stronger and why ?

Sec. 6.16. **8.** Explain the terms bond length, bond energy and bond angle.

9. Briefly explain quantum theory of covalent bond formation.

Sec.6.17. to 6.20. **10.** What do you understand by partial ionic character of covalent bond ? How is it calculated ? Explain taking example of HCl, given that its observed dipole moment is 1·03 D and bond length is 1·275 Å.

11. Define dipole moment. Discuss its important applications.

12. Why are some covalent bonds polar ? What is a dipole ? How can a molecule that has polar bonds be a non-polar molecule ? How do dipole moments of molecules of CO_2, CH_4, H_2O and NH_3 help in ascertaining their structure ?

Sec.6.21. to 6.22. **13.** List various characteristics of covalent compounds. Differentiate between electrovalent and covalent compounds.

Sec.6.23. to 6.25. **14.** What is meant by hybridisation of atomic orbitals ? How does it explain the shapes of molecules ? Illustrate your answer with suitable examples.

15. What is VSEPR theory ? How does it explain the bond angles observed in CH_4, NH_3 and H_2O molecules?

Sec 6.26. **16.** What is a co-ordinate bond ? Explain the formation of a co-ordinate bond. Describe it in orbital overlap concept taking an example.

Sec 6.27. **17.** What is Resonance ? Explain with a suitable example. Define Resonance energy.

Sec 6.28. **18.** What is a hydrogen bond ? What requirements should a molecule fulfil for the formation of hydrogen bond ? Explain the formation of hydrogen bond in HF and NH_3 molecules. Discuss intramolecular hydrogen bond.

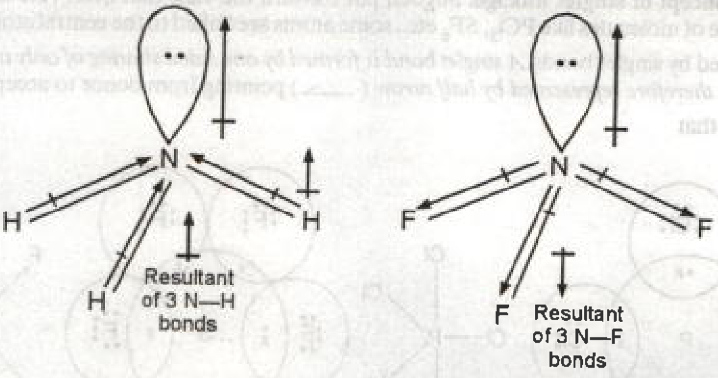
COMPETITION FOCUS

ADDITIONAL USEFUL INFORMATION

1. Comparison of dipole moments of NH_3 and NF_3 - A typical case. Both NH_3 and NF_3 molecules have pyramidal shapes with one lone pair of electrons on N atom. As fluorine is highly electronegative, it appears that N—F bond should be more polar and the net dipole moment of NF_3 should be much greater than that of NH_3. However, actually the dipole moment of NF_3 (0·24 D or $0{\cdot}80 \times 10^{-30}$ Cm) is much smaller than that of NH_3 (viz 1·46 D or $4{\cdot}90 \times 10^{-30}$ Cm). This is explained on the basis of the following two reasons.

(*i*) The dipole formed between the lone pair and N atom has to be taken into consideration which is in the direction of the lone pair.

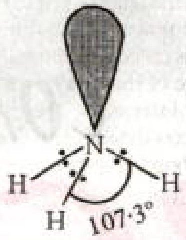
(*ii*) F is more electronegative than N, therefore direction of bond is from N to F whereas N is more electronegative than H, the direction of the bond is from H to N (It may be noted that electronegativity difference between N and H *i.e.* 3·0 − 2·1 = 0·9 and between N and F *i.e.* 4·0 − 3·0 = 1·0 is nearly same)

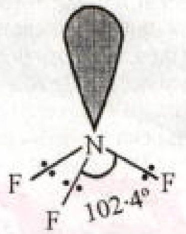


Thus whereas resultant moment of N—H bonds adds up to the bond moment of lone pair, that of 3 N—F bonds partly cancels the resultant moment of lone pair. Hence the net dipole moment of NF_3 is less than that of NH_3.

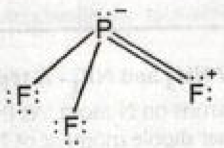
2. Comparison of bond angles of NH_3 and NF_3. Both NH_3 and NF_3 are pyramidal in shape with one lone pair on N. However as F has higher electronegativity than H, the electron pair is attracted more towards F in NF_3 *i.e.* the bond pairs of electrons are away from N or in other words, distance between bond pairs is more. Hence repulsions between the bond pairs in NF_3 is less than in NH_3. Hence the lone pair repels the bond pairs of NF_3 more than it does in NH_3. As a result, the bond angle decreases to 102·4° whereas in NH_3, it decreases to 107·3° only.

ADDITIONAL USEFUL INFORMATION contd.



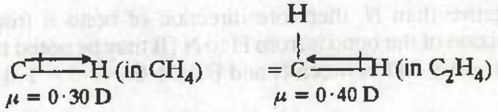


Note. PH_3 and PF_3 are also pyramidal in shape with one lone pair on P. But PF_3 has greater bond angle than PH_3 (opposite to NH_3 and NF_3). This is due to resonance in PF_3 leading to partial double bond character as shown below :



As a result, repulsions between P—F bonds are large and hence the bond angle is large. There is no possibility for the formation of double bonds in PH_3.

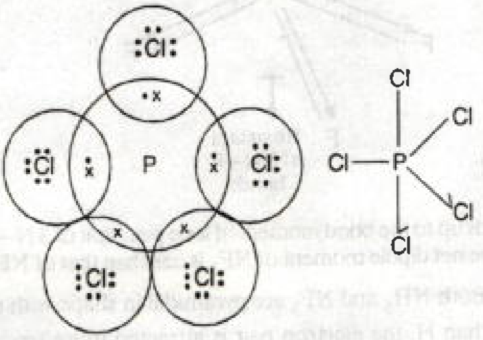
3. Effect of the type of hybridisation on the direction of polarity of a bond and magnitude of dipole moment. For example, the direction and magnitude of dipole moment of C—H bond in methane and ethylene are as follows :

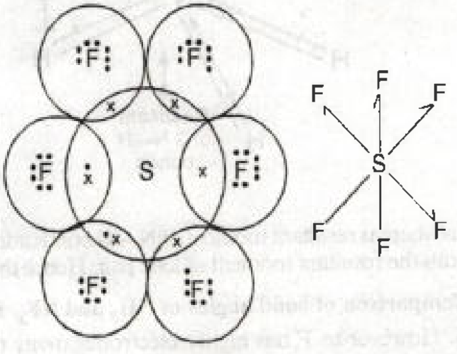


$$\underset{\mu = 0\cdot 30\text{ D}}{C \longleftarrow H \text{ (in } CH_4)} \qquad \underset{\mu = 0\cdot 40\text{ D}}{=\overset{H}{\overset{|}{C}} \longleftarrow H \text{ (in } C_2H_4)}$$

4. Sugden's concept of singlet linkage. Sugden put forward the view that octet rule is never violated. He suggested that in case of molecules like PCl_5, SF_6 etc., some atoms are linked to the central atom by covalent bonds while others are linked by singlet bonds. *A singlet bond is formed by one sided sharing of only* **one electron** *between the two atoms and is therefore represented by half arrow* (⇀) pointing from donor to acceptor. Thus we have

It can be seen that





No. of singlet bonds = Total no. of bonds—No. of electrons required to complete the octet.

5. Polarising power and Polarisability (Fajan's Rules). Although in an ionic compound, the bond is considered to be 100% ionic, actually it has some covalent character. Thus just as covalent bond has some ionic character, ionic bonds have some covalent character. This was explained by Fajan as follows :

ADDITIONAL USEFUL INFORMATION contd.

When a cation approaches an anion, the electron cloud of the anion is attracted towards the cation and hence gets distorted. The effect is called **polarisation** of the anion. The power of the cation to polarise the anion is called its **polarising power** and the tendency of the anion to get polarised is called its **polarisability.** The greater is the polarisation produced, more is the neutralisation of the charges (*i.e.* charge of the cation by the electron cloud of the anion) and hence the ionic character decreases or the covalent character increases. The properties like melting point, heat of sublimation, solubility in water or non-polar solvents change accordingly. The polarising power of the cation and the polarisability of the anion and hence the formation of covalent bond is favoured by the following factors:

(i) Small size of the cation. *Smaller the cation, greater is its polarising power.* This explains why LiCl is more covalent than KCl.

(ii) Large size of the anion. *Larger the anion, greater is its polarisabiliy* (because the hold on the electron cloud by the nucleus decreases). This explains why covalent character of lithium halides is in the order

$$\mathrm{LiI > LiBr > LiCl > LiF}$$

That is why their melting points are in the order

$$\underset{(446°\,C)}{\mathrm{LiI}} < \underset{(547°\,C)}{\mathrm{LiBr}} < \underset{(613°\,C)}{\mathrm{LiCl}} < \underset{(870°\,C)}{\mathrm{LiF}}$$

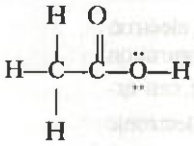
(iii) Large charge on the cation or anion. *Larger the charge on the cation, greater is its polarising power* (because the electron cloud of the anion is more easily and strongly attracted by the cation). Hence covalent character increases. That is why the covalent character of the chlorides is in the order

$$\mathrm{Na^+Cl^- < Mg^{2+}Cl_2 < Al^{3+}Cl_3}.$$

Similarly, greater the charge on the anion, more easily it gets polarised.

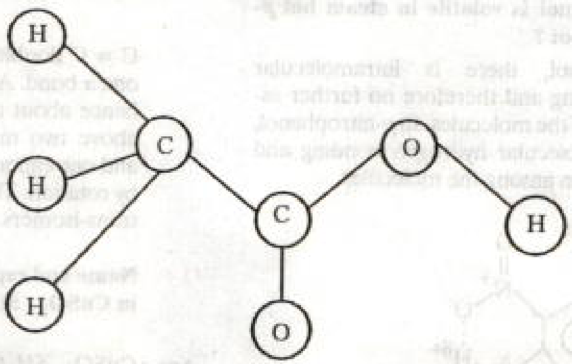
(iv) Electronic configuration of the cation. If two cations have the same size and charge, then the *one with pseudo noble gas configuration* (with 18 electrons in the outermost shell) *has greater polarising power than the other with noble gas configuration* (with 8 electrons in the outermost shell). This explains why $\mathrm{Cu^+Cl^-}$ is more covalent than $\mathrm{Na^+Cl^-}$.

6. Application of VSEPR theory to complex molecules i.e. not having only one central atom. Let us explain by taking the example of acetic acid. Its Lewis structure is



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

The first C—atom on the left has 4 bond pairs only, therefore its geometry is tetrahedral. The second C—atom (central C—atom) has 3 bond pairs (counting double bond as one bond pair). So its geometry is trigonal planar. The next atom viz O- atom has 2 bond pairs and 2 lone pairs. So it has a bent geometry. Combining all these geometries, we get the overall geometry of acetic acid as follows :

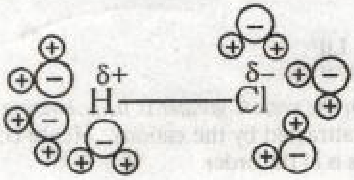


The above structure can also be written on the basis of hybridisation. Hybridisation involved will be : 1st C—atom, sp^3, 2nd C-atom, sp^2, next O-atom, sp^3 (with two orbitals containing lone pairs of electrons).

C.B.S.E.-P.M.T. (MAINS) SPECIAL

Q. 1. Why is HCl predominantly covalent in the gaseous state but ionic in the aqueous solution?

Ans. The electronegativity difference between Cl and H atoms is 3·0 − 2·1 = 0·9. Hence HCl is predominantly covalent in the gaseous state. However, being a polar molecule $(\overset{\delta+}{H}—\overset{\delta-}{Cl})$, when dissolved in water, the polar H_2O molecules interact with HCl molecule as follows :



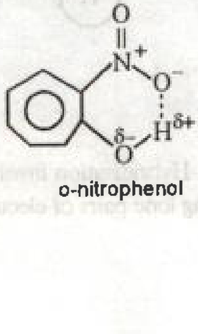
As a result, the bond between H and Cl is broken and we get hydrated H^+ and Cl^- ions in the solution.

Q. 2. Why PCl_5 exists but NCl_5 does not ?

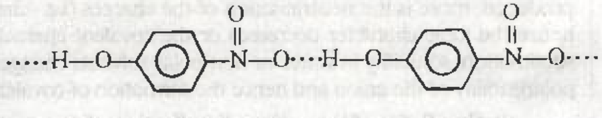
Ans. Electronic configuration of $_{15}P$ is $1s^2\, 2sp^2\, 2p^6\, 3s^2\, 3p_x^1\, 3p_y^1\, 3p_z^1$. Thus the 3*d* orbitals of the valence shell are empty. Hence an electron from 3*s* can jump to 3*d*, giving the configuration $1s^2\, 2s^2\, 2p^6\, 3s^1\, 3p_x^1\, 3p_y^1\, 3p_z^1\, 3d^1$. Thus it can extend its covalency to 5. In case of $_7N$, electronic configuration is $1s^2\, 2s^2\, 2p_x^1\, 2p_y^1\, 2p_z^1$. As there is no 2*d* orbital, it cannot extend its covalency to 5.

Q. 3. Why *o*-nitrophenol is volatile in steam but *p*-nitrophenol is not ?

Ans. In *o*-nitrophenol, there is intramolecular hydrogen bonding and therefore no further association among the molecules. In *p*-nitrophenol, there is intermolecular hydrogen bonding and hence association among the molecules.



o-nitrophenol

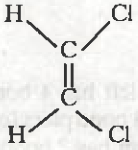


p-nitrophenol

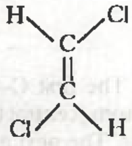
As a result, boiling point of *o*-nitrophenol is less and hence is volatile in steam but boiling point of *p*-nitrophenol is high and hence is not volatile in steam.

Q. 4. Explain how the valence bond theory explains the existence of cis and trans isomers.

Ans. According to valence bond theory, a covalent bond is formed by overlap of half-filled atomic orbitals. If overlap is along the intermolecular axis, the bond formed is called σ-bond and if the overlap is perpendicular to the internuclear axis, the bond formed is called π-bond. In case of molecules containing C = C double bond with two different atoms or groups attached to each doubly bonded C-atoms, they can exist in two different spatial arrangements, called *cis* and *trans* (or geometrical isomers). For example, for the molecule ClCH = CHCl (1, 2-dichloro ethene), we have



cis-1, 2-dichloro ethene

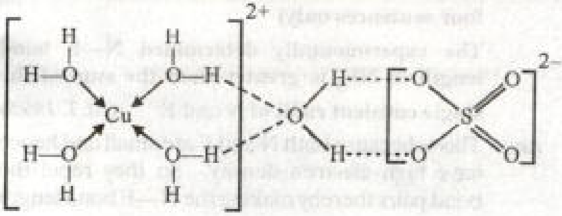


trans-1, 2-dichloroethene

C = C double bond consists of one σ bond and one π bond. As free rotation about a π bond and hence about a double bond is not possible, the above two molecules are completely different and one cannot be changed into the other simply by rotation. This explains the existence of cis and trans-isomers.

Q. 5. 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 below :



Note that four H_2O molecules are linked to Cu^{2+} cation by co-ordinate bonds whereas fifth H_2O molecule is linked by hydrogen bonds between a coordinated H_2O molecule and sulphate ion.

Q. 6. **Give reasons for the following :-**

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

(*ii*) Water molecules have bent structure whereas carbon dioxide molecules are linear.

(*iii*) Ethylene molecules are planar.

(I.S.M. Dhanbad 1990)

Ans. (*i*) In covalent bond, the shared electron pairs are localized between the two atoms or a covalent bond is formed by the overlap of half-filled atomic orbitals which have definite directions. Hence covalent bond is directional. In ionic compounds, each ion is surrounded by a number of oppositely charged ions and there is no definite direction.

(*ii*) H_2O molecule has a net dipole moment whereas dipole moment of CO_2 is found to be zero. Also central atom O in H_2O is sp^3 hybridized whereas central atom C in CO_2 is *sp*-hyrbidized.

(*iii*) This is because each C-atom involves sp^2-hybridisation.

Q. 7. **Taking carbon (atomic number 6) as an example, explain the meaning of valence electrons.**

(B.I.T. Ranchi 1991)

Ans. The electrons present in the outermost shell are called valence electrons because they tell about the valency of the atom *e.g.* in case of C-atom, E.C. is 2, 4. Hence its valency is 4.

Q. 8. **Explain the following :**

(*i*) AlF_3 is a high melting solid wheres SiF_4 is a gas.

(*ii*) H_2S having high molecular weight is a gas whereas H_2O is a liquid.

(I.S.M. Dhanbad 1992)

Ans. (*i*) AlF_3 is an ionic solid due to large difference in electronegativties of Al and F whereas SiF_4 is a covalent compound and hence there are only weak van der Waal's forces among their molecules.

(*ii*) There is hydrogen bonding in H_2O but no hydrogen bonding in H_2S.

I.I.T. (MAINS) SPECIAL

A. SUBJECTIVE QUESTIONS

Q. 1. **Explain the following on the basis of valence bond theory**

(*i*) BF_3 is planar but NH_3 is not

(*ii*) CCl_4 and $SiCl_4$ are tetrahedral

(*iii*) The HSH bond angle in H_2S is closer to 90° than HOH bond angle in H_2O

Ans. (*i*) In BF_3, B-atom undergoes sp^2 hybridisation. Hence BF_3 is triangular planar. In NH_3, N-atom undergoes sp^3 hybridisation. Hence NH_3 has pyramidal shape with one lone pair on N-atom.

(*ii*) Both C in CCl_4 and Si in $SiCl_4$ undergo sp^3 hybridisation. Hence they are tetrahedral.

(*iii*) Refer to page 6/44.

Q. 2. **In each of the following pairs of compounds, which one is more covalent and why ?**

(*i*) AgCl, AgI (*b*) $BeCl_2$, $MgCl_2$

(*iii*) $SnCl_2$, $SnCl_4$ (*iv*) CuO, CuS

Ans. Applying Fajan's rules, the result can be obtained in each case, as follows :

(*i*) AgI is more covalent than AgCl. This is because I^- ion is larger in size than Cl^- ion and hence is more polarized than Cl^- ion.

(*ii*) $BeCl_2$ is more covalent than $MgCl_2$. This is because Be^{2+} ion is smaller in size than Mg^{2+} ion and hence has greater polarizing power.

(*iii*) $SnCl_4$ is more covalent than $SnCl_2$. This is because Sn^{4+} ion has greater charge and smaller size than Sn^{2+} ion and hence has greater polarizing power.

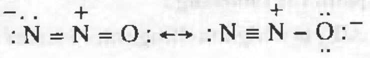
(*iv*) CuS is more covalent than CuO. This is because S^{2-} ion has larger size than O^{2-} ion and hence is more polarized than O^{2-} ion.

Q. 3. Giving reasons in brief, indicate whether the following statements is TRUE or FALSE.

The presence of polar bonds in a polyatomic molecule suggests that the molecule has non-zero dipole moment. ***(I.I.T. 1990)***

Ans. False because in symmetrical polyatomic molecules like BF_3, CH_4, CCl_4 etc., bond moments cancel out and the net dipole moment is zero.

Q. 4. Write two resonating structures of N_2O that satisfy the octet rule. ***(I.I.T. 1990, M.L.N.R. Allahabad 1993)***

Ans. 

$$\overset{-}{:\ddot{N}} = \overset{+}{N} = O: \longleftrightarrow :N \equiv \overset{+}{N} - \ddot{\underset{..}{O}}:^{-}$$

Q. 5. Arrange the following in order of increasing strength of hydrogen bonding (X.........H—X).

O, F, S, Cl, N

(I.I.T. 1991, M.L.N.R. Allahabad 1993)

Ans. Cl < S < N < O < F.

Q. 6. Write two resonance structures of ozone which satisfy the octet rule. ***(I.I.T. 1991)***

Ans. See page 6/48.

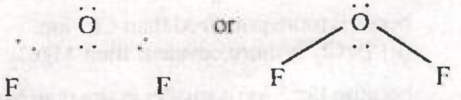
Q. 7. Indicate whether the following statement is TRUE or FALSE. Justify your answer in not more than three lines :

The dipole moment of CH_3F is greater than that of CH_3Cl ***(I.I.T. 1993)***

Ans. False because no doubt 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.

Q. 8. Using the VSEPR theory, identify the type of hybridisation and draw the structure of OF_2. What are oxidation states of O and F ? ***(I.I.T. 1994)***

Ans. Electron dot structure of OF_2 is



Thus the central atom (O-atom) has 4 pairs of electrons (2 bond pairs and 2 lone pairs). Hence oxygen in OF_2 is sp^3 hybridised and the molecule is V-shaped.

Oxidation state of F=—1, Oxidation state of O = +2.

Q. 9. Account for the following : (Write the answer in four sentences only)

The experimentally determined N—F bond length in NF_3 is greater than the sum of the single covalent radii of N and F. ***(I.I.T. 1995)***

Ans. This is because both N and F are small and hence have high electron density. So they repel the bond pairs thereby making the N—F bond length larger.

Q. 10. Give reason for the following :

The molecule of $MgCl_2$ is linear while that of stannous chloride is angular. ***(M.L.N.R. Allahabad 1995)***

Ans. E.C. of $_{12}Mg$ is $1s^2\,2s^2\,2p^6\,3s^2$ in the ground state. Hence in the excited state, it is $1s^2\,2s^2\,2p^6\,3s^1\,3p_x^1$. It undergoes *sp*-hybridisation. Therefore the shape of $MgCl_2$ is linear E.C. of Sn is [Kr] $5s^2\,5p_x^1\,5p_y^1$. It undergoes sp^2-hybridisation. The two half-filled hybrid orbitals form bonds with Cl-atoms while the third is occupied by a lone pair. Hence $SnCl_2$ is bent or V-shaped.

Q. 11. Explain why the dipole moment of NH_3 is more than that of NF_3? ***(Roorkee 1995)***

Ans. Refer to page 6/68.

Q. 12. Explain why bond angle of NH_3 is greater than that of NF_3 while bond angle of PH_3 is less than that of PF_3.

Ans. Refer to page 6/68, 6/69.

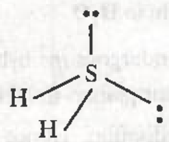
Q. 13. Interpret the non-linear shape of H_2S and non-planar shape of PCl_3 using valence shell electron pair repulsion (VSEPR) theory. ***(I.I.T. 1998)***

Ans. H_2S

No. of electron pairs around S

$$= \frac{6+2}{2} = \frac{8}{2} = 4$$

So hybridisation = sp^3



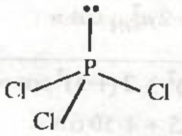
(V- shaped or angular)

PCl_3

No. of electron pairs around P

$$= \frac{5+3}{2} = \frac{8}{2} = 4$$

So hybridisation = sp^3



(Trigonal pyramidal shape)

Q. 14. Which of the following has larger dipole moment ? Explain.

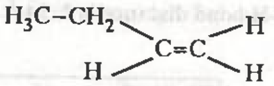
1-Butyne or 1-Butene *(Roorkee 1999)*

Ans. Their structures are

$H_3C{-}CH_2{-}C{\equiv}C{-}H$

1−Butyne

Each triply bonded C-atom is *sp*-hybridized



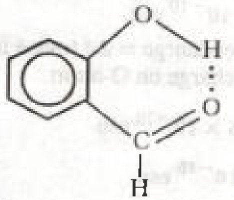
1−Butene

Each doubly C-atom is sp^2-hybridized.

1-Butyne has larger dipole moment because the electronegativity of *sp*-C is more than that of sp^2 − C.

Q. 15. Explain why *o*-hydroxybenzaldehyde is a liquid at room temperature while *p*-hydroxy benzaldehyde is a high melting solid. *(I.I.T. 1999)*

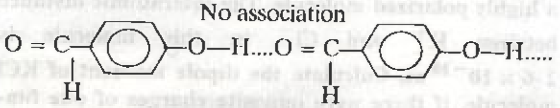
Ans. In *o*-hydroxy benzaldehyde, there is intramolecular hydrogen bonding and hence there is no further association among the molecules *i.e.* they exist as single molecules. In case of *p*-hydroxy benzaldehyde, there is intermolecular hydrogen bonding and hence the molecules are associated through hydrogen bonding



o-hydroxy benzaldehyde

Intramolecular-bonding

No association



p-hydroxy benzaldehyde

Intermolecular H-bonding

Association through H-bonding

As a result, *o*-hydroxy benzaldehyde is a liquid while *p*-hydroxy benzaldehyde is a high melting solid.

Q. 16. Why HCl is polar while Cl_2 molecule is non-polar ? *(B.I.T. Ranchi 2000)*

Ans. In Cl_2 (Cl—Cl) both atoms have same electronegativity. Hence the shared pair of electrons is attracted equally by both and remains exactly in the centre. No end acquires positive or negative charge. In HCl, Cl is more electronegative than H. Hence shared pair of electrons is more attracted towards Cl which, therefore, acquires negative charge while H acquires positive charge.

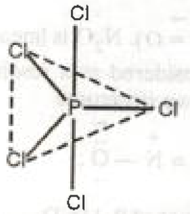
Q. 17. Which one of NF_3 and NH_3 is more polar and why ? *(West Bengal J.E.E. 2001)*

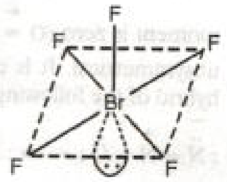
Ans. The electronegativity difference between N and H and that between N and F is nearly same, yet NH_3 is more polar than NF_3. Reason discussed on page 6/68.

Q. 18. Using VSEPR theory, draw the shapes of PCl_5 and BrF_5. *(I.I.T. 2003)*

Ans. (*i*) In PCl_5, number of electrons in the valence shell of the central atom viz. P = 5. These are shared with 5 Cl atoms. Thus there are 5 bond pairs and no lone pair on the central atom. Therefore, the hybridization is sp^3d and the shape is *trigonal bipyramidal.*

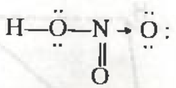
In BrF_5, number of electrons in the valence shell of the central atom viz. Br = 7. Five out of these are shared with 5 Br atoms. Thus there are 5 bond pairs and one lone pair. Hence, hybridization is $sp^3\,d^2$ and the shape is *square pyramidal*



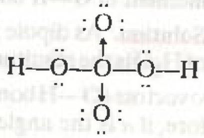


Q. 19. What is the S.I. unit of dipole moment ? Draw the Lewis dot diagrams of nitric acid, sulphuric acid, phosphorous acid and hypophosphorous acid. *(West Bengal J.E.E. 2003)*

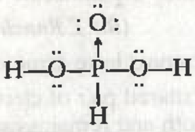
Ans. The S.I. unit of dipole moment is Coulomb metre (Cm), 1 Debye = $3{\cdot}335 \times 10^{-30}$ Cm. Lewis dot structures of the given acids are as follows :



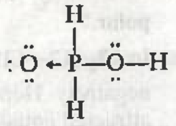
Nitric acid



Sulphuric acid



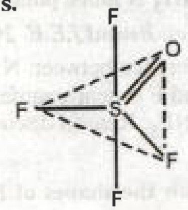
Phosphorous acid



Hypophosphorous acid

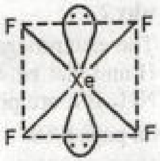
Q. 20. Using VSEPR theory, draw the molecular structures of OSF_4 and XeF_4 indicating the location of lone pair (*s*) of electrons and hybridisation of central atoms. *(I.I.T. 2004)*

Ans.



Trigonal lipyramidal

(sp^3d hybridisation)



Square planar

(sp^3d^2 hybridisation)

Q. 21. State with reasons

(i) Which is more acidic—anhydrous HCl or aqueous HCl ?

(ii) Which is more polar —CO_2 or N_2O ?

(iii) Which is more volatile-ortho nitrophenol or para nitrophenol ? *(West Bengal J.E.E. 2004)*

Ans. (*i*) Aqueous HCl is more acidic. For reason see Ans. to Q. 1, pag 6/71.

(*ii*) N_2O is more polar than CO_2. This is because CO_2 is linear and symmetrical. Its net dipole moment is zero ($O \overset{\leftarrow}{=} C \overset{\rightarrow}{=} O$). N_2O is linear but unsymmetrical. It is considered as a resonance hybrid of the following two structures

$$:\overset{-}{\ddot{N}} = \overset{+}{N} = \ddot{O}: \longleftrightarrow :N \equiv \overset{+}{N} - \overset{-}{\underset{..}{\ddot{O}}}:$$

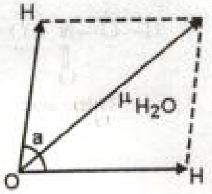
It has a net dipole moment of 0·116 D.

(*iii*) *o*-nitrophenol is more volatile. For reason, see Ans. to Q. 3, page 6/71.

B. PROBLEMS

Problem 1. **The observed value of dipole moment of H_2O molecule is found to be 1·84 D. Calculate the H—O—H bond angle in H_2O molecule, given that the bond moment of O—H bond is 1·5 D.**

Solution. As dipole moment of H_2O is the resultant of the two vectors (O—H bonds), therefore, if α is the angle between the two vectors, then



$$\mu = \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cos \alpha}$$

$$\mu_{H_2O} = \sqrt{\mu_{OH}^2 + \mu_{OH}^2 + 2\mu_{OH}^2 \cos \alpha}$$

$$1·84 = \sqrt{(1·5)^2 + (1·5)^2 + 2(1·5)^2 \cos \alpha}$$

or $3·3856 = 2·25 + 2·25 + 4·50 \cos \alpha$

or $\cos \alpha = -0·2476$

or $\alpha = 104° \, 20'$

[$\cos (180 - \theta) = -\cos \theta$

i.e. $\cos (180 - \alpha) = 0·2476$]

Problem 2. **Taking the HOH bond angle in H_2O molecule as 105°, calculate the charge on oxygen atom. Given that the dipole moment of H_2O molecule is 1·84 D and O—H bond distance is 0·94 Å.**

Solution.

$$\mu_{H_2O} = \sqrt{\mu_{OH}^2 + \mu_{OH}^2 + 2\mu_{OH}^2 \cos 105°}$$

$$\therefore (1·84)^2 = 2\mu_{OH}^2 + 2\mu_{OH}^2 \times (0·2588)$$

$$3·3856 = 2\mu_{OH}^2 (1 - 0·2588)$$

[$\cos 105° = \cos (180 - 75°) = -\cos 75°$]

$$= 1·4824 \, \mu_{OH}^2$$

or $\mu_{OH}^2 = 2·2839$

or $\mu_{OH} = 1·51 \text{ D} = 1·51 \times 10^{-18}$ esu cm.

But μ_{O-H} = Charge (δ) × d

$\therefore$ $1·51 \times 10^{-18}$ esu cm $= \delta \times (0·94 \times 10^{-8}$ cm)

or $\delta = 1·606 \times 10^{-10}$ esu.

As O atom acquires charge $= 2\delta$ (one δ from each O—H bond) therefore charge on O-atom

$= 2 \times 1·606 \times 10^{-10}$ esu

$= 3·212 \times 10^{-10}$ esu.

Problem 3. **The dipole moment of KCl is $3·336 \times 10^{-29}$ coulomb metre which indicates that it is a highly polarized molecule. The interatomic distance between K^+ and Cl^- in this molecule is $2·6 \times 10^{-10}$ m. Calculate the dipole moment of KCl molecule, if there were opposite charges of one fundamental unit located at each nucleus. Calculate the percentage ionic character of KCl.** *(I.I.T. 1993)*

Solution. If there were opposite charges of one fundamental unit *i.e.* $q = 1·602 \times 10^{-19}$ coulombs, then

$$\mu = q \times d$$

$= (1 \cdot 602 \times 10^{-19}$ coulombs$) \times (2 \cdot 6 \times 10^{-10}\ m)$

$= 4 \cdot 1652 \times 10^{-29}$ **coulomb metre**

$\mu_{observed} = 3 \cdot 336 \times 10^{-29}$ columb metre

$\therefore$ % ionic character

$$= \frac{3 \cdot 336 \times 10^{-29}}{4 \cdot 1652 \times 10^{-29}} \times 100 = \mathbf{80 \cdot 09\%}$$

Problem 4. **Calculate the electronegativity of flourine from the following bond energy data :**

$E_{H-H} = 104 \cdot 2$ kcal mol^{-1},

$E_{F-F} = 36 \cdot 6$ kcal mol^{-1},

$E_{H-F} = 134 \cdot 6$ kcal mol^{-1} *(M.L.N.R. 1996)*

Solution. Suppose the electronegativities of H and F are represented as χ_H and χ_F. Applying Pauling's formula,

$|\chi_H - \chi_F| = 0 \cdot 102 \sqrt{\Delta}$ when Δ is in kJ mol^{-1}

$$\Delta = BE\,(H-F) - \frac{BE\,(H-H) + BE\,(F-F)}{2}$$

$$= 134 \cdot 6 - \frac{104 \cdot 2 + 36 \cdot 6}{2} \text{ kcal mol}^{-1}$$

$= 64 \cdot 2$ kcal mol^{-1} $= 268 \cdot 6$ kJ mol^{-1}

$\therefore |\chi_H - \chi_F| = 0 \cdot 102 \sqrt{268 \cdot 6} = 1 \cdot 67$

As $\chi_F > \chi_H$, $\chi_F = 1 \cdot 67 + \chi_H$

$= 1 \cdot 67 + 2 \cdot 1 = 3 \cdot 77 = 3 \cdot 8$

Problem 5. **Anhydrous $AlCl_3$ is covalent. From the data given below, predict whether it would remain covalent or become ionic in aqueous solution (Ionization energy for $AlCl_3$ = 5137 kJ mol^{-1}, $\Delta H_{hydration}$ for Al^{3+} = –4665 kJ mol^{-1}, $\Delta H_{hydration}$ for Cl^- = –381 kJ mol^{-1}.)**

(I.I.T. 1997)

Solution. $AlCl_3\ (s) + aq \longrightarrow AlCl_3\ (aq) \longrightarrow$

$Al^{3+}\ (aq) + 3Cl^-\ (aq)$

Total energy released on hydration of 1 mole of Al^{3+} ions and 3 moles of Cl^- ions

$= 4665 + 3 \times 381$ kJ $= 5808$ kJ mol^{-1}

Energy required for ionization = 5137 kJ mol^{-1}

As energy released is greater than the energy required, hence the compound will ionize in aqueous solution.

MULTIPLE CHOICE QUESTIONS

For CBSE– PMT (Preliminary), IIT Screening, AIEEE, AIIMS, AFMC, DPMT, CPMT, BHU and All Other Competitive Examinations

1. A polar covalent bond is formed by
   (*a*) transference of one electron
   (*b*) transference of one or more electrons
   (*c*) sharing of one electron
   (*d*) sharing of one or more electrons.

2. Dipole moment of BeF_2 is
   (*a*) very low (*b*) very high
   (*c*) zero (*d*) not definite.

3. Carbon in ethylene involves the hybridisation
   (*a*) sp^3 (*b*) sp^2
   (*c*) sp (*d*) none of these.

4. Hybridisation involves
   (*a*) orbitals of same atom with slightly different energies
   (*b*) orbitals of different atoms but with equal energies
   (*c*) orbitals of same atom but with widely different energies
   (*d*) orbitals of different atoms with different energies
   (*e*) orbitals of the same atom with exactly equal energies.

5. Which of the following statements is wrong ?
   (*a*) Covalent compounds are generally soluble in polar solvents
   (*b*) Covalent compounds have low melting and boiling points
   (*c*) Ionic solids do not conduct electricity
   (*d*) Ionic compounds conduct electricity in the fused state.

✓6. ✓CO_2 is isostructural with (one or more)
   [✓ (*a*)] $HgCl_2$ (*b*) $SnCl_2$

ANSWERS

1. *d* 2. *c* 3. *b* 4. *a* 5. *a*

[✓ (c) C_2H_2] (d) NO_2 *(I.I.T. 1986)*

7. Dipole moment is possessed by (one or more)
(a) 1, 4-Dichlorobenzene
[✓ (b) *cis* 1, 2-Dichloroethene]
(c) *trans* 1, 2-Dichloroethene
[✓ (d) *trans*-1, 2, Dichloro-2-pentene.] *(I.I.T. 1986)*

8. Which of the following contains both covalent and ionic bonds ?
(a) CCl_4 (b) $CaCl_2$
[✓ (c) NH_4Cl] (d) H_2O.
(M.L.N.R. Allahabad 1990)

9. Which of the following contains a coordinate bond ?
[✓ (a) $N_2H_5^+$] (b) $BaCl_2$
(c) HCl (d) H_2O.
(M.L.N.R. Allahabad 1990)

10. In which of the following the central atom does not use sp^3-hybrid orbitals in its bonding.
[✓ (a) BeF_3^-] (b) OH_3^+
(c) NH_2^- (d) NH_3
(M.L.N.R. Allahabad, 1990)

11. The molecule which does not exhibit dipole moment is :
(a) NH_3 (b) $CHCl_3$
(c) H_2O [✓ (d) CCl_4.]
(M.L.N.R. Allahabad 1991)

12. What is the maximum number of hydrogen bonds in which a water molecule can participate ?
(a) 1 (b) 2
(c) 3 [✓ (d) 4.]
(M.L.N.R. Allahabad 1991, I.I.T. 1992, M.P. C.E.E. 1999)

13. The linear structure is assumed by (one or more)
(a) $SnCl_2$ [✓ (b) NCO^-]
(c) NO_2^+ [✓ (d) CS_2.] *(I.I.T. 1991)*

14. The molecules that will have dipole moment (one or more)
(a) 2, 2-Dimethyl propane
[✓ (b) trans-2-Pentene]
[✓ (c) cis-3-Hexene]
(d) 2, 2, 3, 3-tetramethyl butane. *(I.I.T. 1992)*

15. Which one of the following has zero dipole moment ?
(a) ClF (b) PCl_3
[✓ (c) SiF_4] (d) $CFCl_3$. *(I.I.T. 1993)*

16. Two lone pairs of electrons and two bond pairs of electrons are present in
(a) NH_3 (b) BF_3
[✓ (c) H_2O] (d) CO_2 *(C.P.M.T. 1993)*

17. H_2O has higher boiling point than H_2S because
(a) H_2O is a smaller molecule and hence more closely packed.
(b) the bond angle in H_2O is more than in H_2S and hence the former molecules are more tightly packed.
[✓ (c) of intermolecular hydrogen bonding in liquid H_2O]
(d) the latent heat of vaporisation is higher for water than for H_2S. *(I.S.M. Dhanbad, 1994)*

18. The central atom assumes sp^3-hybridisation in
[✓ (a) PCl_3] (b) SO_3
(c) BF_3 (d) NO_3^-
(M.L.N.R. Allahabad 1994)

19. NH_3 and BF_3 form an adduct readily because they form
(a) an ionic bond (b) a covalent bond
[✓ (c) a coordinate bond] (d) a hydrogen bond.
(M.L.N.R. Allahabad 1994)

20. NH_3 has a much higher boiling point than PH_3 because
(a) NH_3 has larger molecular weight
(b) NH_3 undergoes umbrella inversion
[✓ (c) NH_3 forms hydrogen bond.]
(d) NH_3 contains ionic bonds whereas PH_3 contains covalent bonds.
(M.L.N.R. Allahabad, 1994)

21. Which of the following has net dipole moment ?
(a) CCl_4 (b) BF_3
[✓ (c) NH_3] (d) CO_2.
(Haryana C.E.E.T. 1994)

ANSWERS

6. *a,c* **7.** *b,d* **8.** *c* **9.** *a* **10.** *a* **11.** *d* **12.** *d* **13.** *b,d* **14.** *b,c* **15.** *c*
16. *c* **17.** *c* **18.** *a* **19.** *c* **20.** *c* **21.** *c*

22. Hydrogen bonding is maximum in

[✓ (*a*) Ethanol] (*b*) Diethyl ether
(*c*) Ethyl chloride (*d*) Triethyl amine.

(M.L.N.R. 1995)

23. The number and type of bonds between two carbon atoms in CaC_2 are

(*a*) one sigma (σ) and one pi (π) bond
(*b*) one sigma (σ) and two pi (π) bonds
(*c*) one sigma (σ) and one and a half pi (π) bond
[✓ (*d*) one sigma (σ) bond]

24. Which of the following hydrogen halide is most volatile ?

(*a*) HF [✓ (*b*) HCl]
(*c*) HBr (*d*) HI.

(Haryana C.E.E.T. 1996)

25. Among the following species, identify the isostructural pairs NF_3, NO_3^-, BF_3, H_3^+O, HN_3

(*a*) $[NF_3, NO_3^-]$ and $[BF_3, H_3^+O]$
(*b*) $[NF_3, HN_3]$ and $[NO_3^-, BF_3]$
[✓ (*c*) $[NF_3, H_3^+O]$ and $[NO_3^-, BF_3]$]
(*d*) $[NF_3, H_3^+O]$ and $[HN_3, BF_3]$ *(I.I.T. 1996)*

26. Arrange the following compounds in order of increasing dipole moment

Toluene (I), *m*-dichlorobenzene (II), *o*-dichlorobenzene (III), *p*-dichlorobenzene (IV)

(*a*) I < IV < II < III [✓ (*b*) IV < I < II < III]
(*c*) IV < I < III < II (*d*) IV < II < I < III.

(I.I.T. 1996)

27. KF combines with HF to form KHF_2. The compound contains the species

(*a*) K^+, F^- and H^+ (*b*) K^+, F^- and HF
[✓ (*c*) K^+ and $[HF_2]^-$] (*d*) $[KHF]^+$ and F_2.

(I.I.T. 1996)

28. Among the following compounds, the one that is polar and has the central atom with sp^2 hybridisation is

[✓ (*a*) H_2CO_3] (*b*) SiF_4
(*c*) BF_3 (*d*) $HClO_2$.

(I.I.T. 1997, C.P.M.T. 2000)

29. Which contains both polar and non-polar bonds ?

(*a*) NH_4Cl (*b*) HCN
[✓ (*c*) H_2O_2] (*d*) CH_4. *(I.I.T. 1997)*

30. Which one of the following compounds has sp^2 hybridisation ?

(*a*) CO_2 [✓ (*b*) SO_2]
(*c*) N_2O (*d*) CO. *(I.I.T. 1997)*

31. Among KO_2, AlO_2^-, BaO_2 and NO_2^+, unpaired electron is present in

(*a*) NO_2^+ and BaO_2 (*b*) KO_2 and AlO_2^-
[✓ (*c*) KO_2 only] (*d*) BaO_2 only.

(I.I.T. 1997)

32. The cylindrical shape of an alkyne is due to

(*a*) three sigma C—C bonds
(*b*) three π C—C bonds
(*c*) two sigma C—C bonds and one π C—C bond
[✓ (*d*) One sigma C—C bond and two π C—C bonds.]

(C.B.S.E. P.M.T. 1997)

33. Which one of the following has highest dipole moment ?

[✓ (*a*) NH_3] (*b*) PH_3
(*c*) SbH_3 (*d*) AsH_3

(C.B.S.E. P.M.T. 1997)

34. In crystals of which of the following ionic compound would you expect maximum distance between the cenres of cations and anions ?

(*a*) CsF [✓ (*b*) Cs I]
(*c*) Li I (*d*) Li F

(C.B.S.E. P.M.T. 1998)

35. Which of the following statement regarding covalent bond is not true ?

(*a*) The electrons are shared between atoms
[✓ (*b*) The bond is non-directional]
(*c*) The strength of the bond depends upon the extent of overlapping
(*d*) The bond formed may or may not be polar.

(M.P. P.M.T. 1998)

36. Hydrogen bonding is not present in

(*a*) Glycerine (*b*) Water
[✓ (*c*) Hydrogen sulphide] (*d*) Hydrogen fluoride.

(M.P. P.M.T. 1998)

37. The geometry and the type of hybrid orbitals present about the central atom in BF_3 is

(*a*) linear, *sp* [✓ (*b*) trigonal planar, sp^2]

ANSWERS

22. *a*	23. *b*	24. *b*	25. *c*	26. *b*	27. *c*	28. *a*	29. *c*	30. *b*	31. *c*
32. *d*	33. *a*	34. *b*	35. *b*	36. *c*					

(c) tetrahedral, sp^3 (d) pyramidal, sp^3.

(I.I.T. 1998 ; Haryana C.E.E.T.)

38. The correct order of increasing C—O bond length of CO, CO_3^{2-}, CO_2 is

(a) $CO_3^{2-} < CO_2 < CO$

(b) $CO_2 < CO_3^{2-} < CO$

(c) $CO < CO_3^{2-} < CO_2$

[✓ (d) $CO < CO_2 < CO_3^{2-}$.] *(I.I.T. 1999)*

39. In a double bond connecting two atoms, there is a sharing of

(a) 2 electrons [✓ (b) 4 electrons]

(c) 1 electron (d) All electrons.

(M.P. C.E.E. 1999)

40. Which one of the following molecules will form a linear polymeric structure due to hydrogen bonding ?

(a) HCl [✓ (b) HF]

(c) H_2O [✓ (d) NH_3.]

(C.B.S.E. P.M.T. 2000)

41. Which among the following has the largest dipole moment ?

[✓ (a) NH_3] (b) H_2O

(c) HI (d) SO_3.

(A.I.I.M.S. 2000)

42. Atomic orbitals of carbon in carbon dioxide are

[✓ (a) sp-hybridised] (b) sp^3d- hybridised

(c) sp^2-hybridised (d) sp^3- hybridised.

(A.I.I.M.S. 2000)

43. The values of electronegativity of atoms A and B are 1·80 and 4·0 respectively. The percentage of ionic character of A—B bond is

(a) 50% (b) 72·24%

(c) 55·3% (d) 43%.

(D.C.E.E.E. 2000)

44. Amongst H_2O, H_2S, H_2Se and H_2Te, the one with the highest boiling point is

[✓ (a) H_2O because of hydrogen bonding]

(b) H_2Te because of higher molecular weight

(c) H_2S because of hydrogen bonding

(d) H_2Se because of lower molecular weight.

(I.I.T. 2000)

45. 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^2, sp^2, sp^3, dsp^3

(d) dsp^2, sp^3, sp^2, dsp^3 *(I.I.T. 2001)*

46. Which of the following two are iso structural ?

[✓ (a) XeF_2, IF_2^-] (b) NH_3, BF_3

(c) CO_3^{2-}, SO_3^{2-} (d) PCl_5, ICl_5

(C.B.S.E. P.M.T. 2001)

47. In which of the following, bond angle is maximum ?

(a) NH_3 [✓ (b) NH_4^+]

(c) PCl_5 (d) SCl_2

(C.B.S.E. P.M.T. 2001)

48. Which one of the following arrangements of molecules is correct on the basis of their dipole moments ?

(a) $BF_3 > NF_3 > NH_3$ (b) $NF_3 > BF_3 > NH_3$

(c) $NH_3 > BF_3 > NF_3$ [✓ (d) $NH_3 > NF_3 > BF_3$]

(e) $NH_3 = NF_3 > BF_3$ *(Kerala E.E.E. 2001)*

49. Bond dissociation energies of HF, HCl and HBr follow the order

(a) HCl > HBr > HF (b) HF > HBr > HCl

[✓ (c) HF > HCl > HBr] (d) HBr > HCl > HF

(E.A.M.C.E.T. 2001)

50. Covalent compounds have low melting point because

(a) Covalent molecules have definite shape

(b) Covalent bond is weaker than ionic bond

(c) Covalent bond is less exothermic

[✓ (d) Covalent molecules are held by weak van der Waal's forces of attraction] *(K.C.E.T. 2002)*

51. Sulphuric acid provides a simple example of

[✓ (a) co-ordiante bonds]

(b) non-covalent compound

(c) covalent ion

(d) non-covalent ion

(e) none of these *(Kerala M.E.E. 2002)*

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

ANSWERS

37. *b* 38. *d* 39. *b* 40. *d* 41. *b* 42. *a* 43. *b* 44. *a* 45. *b* 46. *a*
47. *b* 48. *d* 49. *c* 50. *d* 51. *a*

(*a*) 2, 2 (*b*) 3, 1
(*c*) 1, 3 [✓ (*d*) 4, 0]
(*C.B.S.E. P.M.T. 2002*)

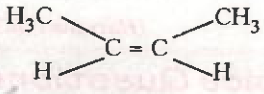
53. In OF_2, number of bond pairs and lone pairs of electrons are respectively
(*a*) 2, 0 [✓ (*b*) 2, 8]
(*c*) 2, 10 (*d*) 2, 9 (*D.P.M.T. 2002*)

54. Which of the following has zero dipole moment ?
(*a*) ClF (*b*) PCl_3
[✓ (*c*) SiF_4] (*d*) $CFCl_3$
(*M.P. P.M.T. 2002*)

55. In which of the following species is the underlined carbon having sp^3-hybridisation ?
(*a*) $CH_3—\underline{C}OOH$ [✓ (*b*) $CH_3\underline{C}H_2OH$]
(*c*) $CH_3—\underline{C}O—CH_3$ (*d*) $CH_2 = \underline{C}H—CH_3$
(*A.I.E.E.E. 2002*)

56. Which of the following does not contain co-ordinate bond ?
(*a*) BH_4^- (*b*) NH_2^-
[✓ (*c*) CO_3^{2-}] (*d*) H_3O^+
(*Rajasthan P.M.T. 2002*)

57. Number of π-bonds in Naphthalene is
(*a*) 6 (*b*) 3
(*c*) 4 [✓ (*d*) 5]
(*Rajasthan P.M.T. 2002*)

58. Which of the following hydrocarbons has the lowest dipole moment ?
(*a*)

(*b*) $CH_3C \equiv CCH_3$
(*c*) $CH_3CH_2C \equiv CH$
(*d*) $CH_2 = CH—C \equiv CH$ (*I.I.T. 2002*)

59. Among the following, the molecule with highest dipole moment is
[✓ (*a*) CH_3Cl] (*b*) CH_2Cl_2
(*c*) $CHCl_3$ (*d*) CCl_4 (*I.I.T. 2003*)

60. 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*)

61. Which of the following statements is not correct for sigma and pi bonds formed between two carbon atoms ?
(*a*) Sigma bond is stronger than pi bond
[✓ (*b*) Bond energies of sigma and pi bonds are of the order of 264 kJ/mol and 347 kJ/mol]
(*c*) Free rotation of atoms about a sigma bond is allowed but not in case of a pi-bond
(*d*) Sigma bond determines the direction between carbon atoms but a pi bond has no primary effect in this regard. (*C.B.S.E. P.M.T. 2003*)

62. Maximum bond angle is present in case of
(*a*) BBr_3 (*b*) BCl_3
(*c*) BF_3 (*d*) same in all
(*D.P.M.T. 2003*)

63. Which of the following pair of molecules will have permanent dipole moment for both members ?
(*a*) NO_2 and CO_2 [✓ (*b*) NO_2 and O_3]
(*c*) SiF_4 and CO_2 (*d*) SiF_4 and NO_2
(*A.I.E.E.E. 2003*)

64. Shape of O_2F_2 is similar to that of
(*a*) C_2F_2 [✓ (*b*) H_2O_2]
(*c*) H_2F_2 (*d*) C_2H_2
(*A.I.I.M.S. 2004*)

65. The ONO bond angle is maximum in
(*a*) NO_3^- (*b*) NO_2^-
(*c*) NO_2 [✓ (*d*) NO_2^+]
(*A.I.I.M.S. 2004*)

66. The dipole moment is highest for
(*a*) trans-2-butene (*b*) 1, 3-dimethyl benzene
[✓ (*c*) acetophenone] (*d*) ethanol
(*A.I.I.M.S. 2004*)

67. Which of the following is arranged in the increasing order of enthalpy of vaporisation ?
(*a*) NH_3, PH_3, AsH_3 (*b*) AsH_3, PH_3, NH_3
(*c*) NH_3, AsH_3, PH_3 [✓ (*d*) PH_3, AsH_3, NH_3]
(*A.I.I.M.S. 2004*)

ANSWERS

52. *d*	**53.** *b*	**54.** *c*	**55.** *b*	**56.** *c*	**57.** *d*	**58.** *b*	**59.** *a*	**60.** *a*	**61.** *b*
62. *d*	**63.** *b*	**64.** *b*	**65.** *d*	**66.** *c*	**67.** *d*				

68. Ionic radii are

(*a*) inversely proportional to effective nuclear charge

(*b*) inversely proportional to the square of the effective nuclear charge

(*c*) directly proportional to effective nuclear charge

(*d*) directly proportional to the square of effective nuclear charge. *(C.B.S.E. P.M.T. 2004)*

69. In BrF_3 molecule, the lone pairs occupy equatorial position to minimize

(*a*) lone pair — bond pair repulsion only

(*b*) bond pair — bond pair repulsion only

(*c*) lone pair — lone pair repulsion and lone pair-bond pair repulsion

(*d*) lone pair — lone pair repulsion only *(C.B.S.E. P.M.T. 2004)*

70. The correct order of bond angles (smallest first) in H_2S, NH_3, BF_3 and SiH_4 is

(*a*) $H_2S < SiH_4 < NH_3 < BF_3$

(*b*) $NH_3 < H_2S < SiH_4 < BF_3$

(*c*) $H_2S < NH_3 < SiH_4 < BF_3$

(*d*) $H_2S < NH_3 < BF_3 < SiH_4$ *(A.I.E.E.E. 2004)*

71. The state of hybridisation of boron and oxygen atoms in boric acid (H_3BO_3) are respectively

(*a*) sp^2 and sp^2 (*b*) sp^2 and sp^3

(*c*) sp^3 and sp^2 (*d*) sp^3 and sp^3 *(A.I.E.E.E. 2004)*

72. Decreasing order of C—C bond length is

I. C_2H_4 II. C_2H_2 III. C_6H_6 IV. C_2H_6

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

(*c*) II > I > IV > III (*d*) IV > I > III > II *(Orissa J.E.E. 2004)*

73. The decreasing order of bond angle is

(*a*) $NO_2 > NO_2^+ > NO_2^-$

(*b*) $NO_2^- > NO_2 > NO_2^+$

(*c*) $NO_2^+ > NO_2 > NO_2^-$

(*d*) $NO_2^+ > NO_2^- > NO_2$ *(J & K C.E.T. 2004)*

74. Which carbon is more electronegative ?

(*a*) sp^3 hybridized carbon

(*b*) sp hybridzed carbon

(*c*) sp^2 hybridized carbon

(*d*) Always same irrespective of its hybrid state

(*e*) None of above *(Kerala C.E.E. 2004)*

75. The H — O — O bond angle is H_2O_2 is

(*a*) 127° 28′ (*b*) 109° 28′

(*c*) 104·5° (*d*) 106°

(*e*) 97° *(Kerala P.M.T. 2004)*

76. If a molecule MX_3 has zero dipole moment, the sigma bonding orbitals used by M are

(*a*) sp^3 *d*-hybrid (*b*) *sp*-hybrid

(*c*) sp^3d^2 hybrid (*d*) sp^3- hybrid

(*e*) sp^2-hybrid *(Kerala P.M.T. 2004)*

77. Which of the following is least volatile ?

(*a*) HF (*b*) HCl

(*c*) HBr (*d*) HI *(Haryana P.M.T. 2004)*

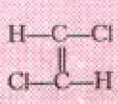
78. Which of the following is not electron deficient ?

(*a*) NH_3 (*b*) BF_3

(*c*) $AlCl_3$ (*d*) BH_3 *(Haryana P.M.T. 2004)*

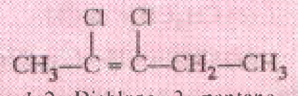
HINTS/EXPLANATIONS to Multiple Choice Questions

1. For example, in O = C = O, each C = O bond is polar and C and O contribute two electrons each for sharing.



$$H{-}C{-}Cl \;\|\; Cl{-}C{-}H$$

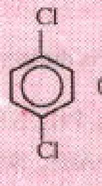
($\mu = 0$),



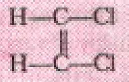
$$CH_3{-}\underset{}{\overset{Cl}{C}}{=}\overset{Cl}{C}{-}CH_2{-}CH_3$$

1, 2–Dichloro–2–pentane

7.



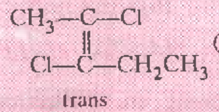
($\mu = 0$),



$$H{-}C{-}Cl \;\|\; H{-}C{-}Cl$$

($\mu \neq 0$),

i.e.



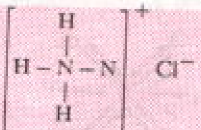
$$CH_3{-}C{-}Cl \;\|\; Cl{-}C{-}CH_2CH_3$$

($\mu \neq 0$)

trans

ANSWERS

68. *a* **69.** *d* **70.** *c* **71.** *b* **72.** *a* **73.** *c* **74.** *b* **75.** *e* **76.** *e* **77.** *a*
78. *a*

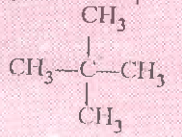
8. 
$\left[\begin{array}{ccc} & H & \\ H- & N- & N \\ & H & \end{array}\right]^{+} Cl^{-}$

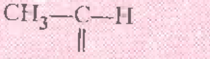
9. $[(NH_2NH_2) \longrightarrow H]^+$

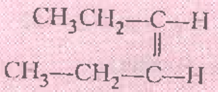
10. BeF_3^- involves *sp*-hybridisation of Be.

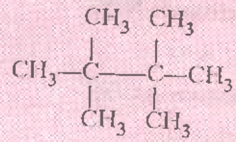
12. Each H_2O molecule can form two H-bonds through O-atom and two H-bonds through two H-atoms (See Fig. 6·51 page 6/55).

13. $[N = C = O]^-$ and $S = C = S$ are linear.

14. 
$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_3$ ($\mu = 0$)

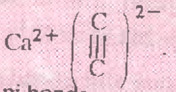

$\begin{array}{c} CH_3-C-H \\ \| \\ H-C-CH_2CH_3 \end{array}$ ($\mu \neq 0$)


$\begin{array}{c} CH_3CH_2-C-H \\ \| \\ CH_3-CH_2-C-H \end{array}$ ($\mu \neq 0$).


$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\overset{CH_3}{\underset{CH_3}{C}}-CH_3$ ($\mu = 0$)

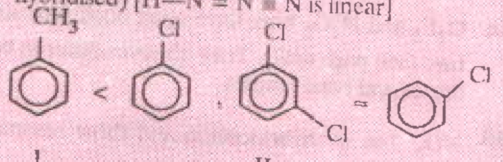
15. SiF_4 is symmetrical molecule. Hence its dipole moment = 0.

18. ${}_{15}P = 1s^2\,2s^2\,2p^6\,3s^2\,3p_x^1\,3p_y^1\,3p_z^1$

23. 
$Ca^{2+}\left(\begin{array}{c} C \\ ||| \\ C \end{array}\right)^{2-}$ sp^3 hybridisation. So it involves one sigma and two pi bonds.

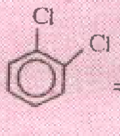
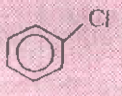
24. Most volatile hydrogen halide is the one which has least boiling point viz HCl.

25. NF_3 and H_3O^+ are pyramidal (sp^3 hybridised) whereas NO_3^- and BF_3 are triangular planar (sp^2 hybridised) [H—N = N ≡ N is linear]

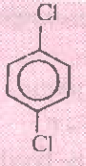
26. 

I

II


= 1·732 times of

,

III


= 0.

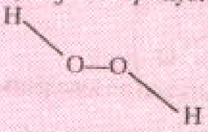
IV

Hence the order is IV < I < II < III.

27. $KHF_2 \longrightarrow K^+ + HF_2^-$.

28. $H_2CO_3 \rightleftharpoons 2\,H^+ + CO_3^{2-}$

(CO_3^{2-} has sp^2 hybridised carbon).

29. 
{O—H is polar bond
O—O is non polar bond.

30. SO_2 is V-shaped molecule with bond angle 119°30′.

31. Electrons present : $NO_2^+ = 7 + 16 - 1 = 22$,

$BaO_2 = 56 + 16 = 72$,

$AlO_2^- = 13 + 16 + 1 = 30$

and $KO_2 = 19 + 16 = 35$

Thus only KO_2 is odd electron species.

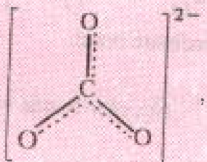
32. For example, H—C ≡ C—H (acetylene). Between two C-atoms, there is one σ-bond and two π-bonds.

33. The N—H bond is most polar. Hence NH_3 has highest dipole moment.

34. Cs^+ ion is largest cation and I^- is largest anion.

35. Covalent bonds are directional.

38. The structures of the given species are

C ≡ O,  , O = C = O.

Thus CO contains triple bond, CO_2 contains double bond while CO_3^{2-} contains between single and double bond. Hence C—O bond lengths will be in the order :

$$CO < CO_2 < CO_3^{2-}$$

41. $\mu(H_2O) = 1·84$ D, $\mu(NH_3) = 1·49$ D. HI and SO_3 are less polar and hence will have less dipole moment.

43. As the difference of electronegativities is 2·2, the % ionic character will be approx 70%.

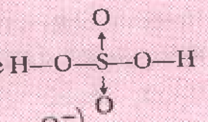
46. Compounds having same shape with same hybridisation of the central atom are called

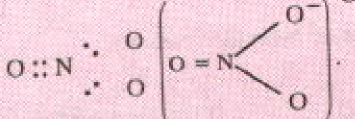
isostructural. Both XeF_2 and IF_2^- are linear species with sp^3d hybridisation of central atom.

47. NH_4^+ is tetrahedral with bond angle 109°28'.

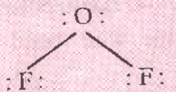
48. $NH_3 > NF_3$ (See page 6/68). $\mu (BF_3) = 0$.

49. Smaller the bond length, greater is the bond dissociation energy.

51. H_2SO_4 has the structure 
$H—O—\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}}—O—H$

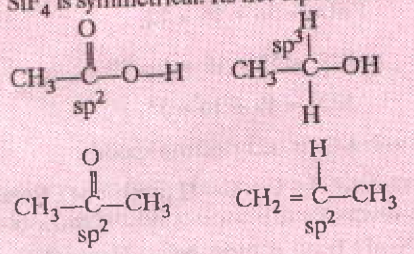
52. 

Thus N has four bond pairs and no lone pairs.

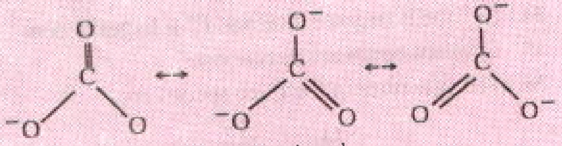
53. 

(2 bond pairs and 8 lone pairs)

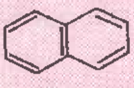
54. SiF_4 is symmetrical. Its net dipole moment = 0.

55. 

56. CO_3^{2-} is

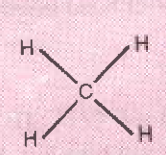


There is no co-ordinate bond.

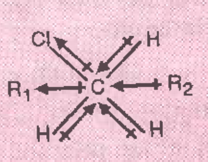
57.  No. of π-bonds = 5.

58. (*b*) is symmetrical with linear structure and therefore, will have zero dipole moment.

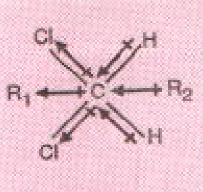
59.



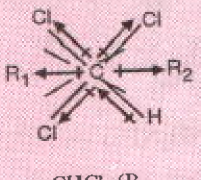
CH_4 (Symmetrical)
$\mu = 0$



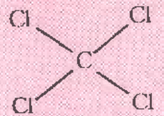
CH_3Cl
(Bond moments C – H, C – Cl reinforce to give resultant R_1
Resultant R_2 further adds up)
$\mu = 1{\cdot}86$ D



CH_2Cl_2 (R_1 is less than R_1 of CH_3Cl. Net resultant is less)
$\mu = 1{\cdot}62$ D



$CHCl_3$ (R_2 opposes R_1)
$\mu = 1{\cdot}03$ D



CCl_4 (Symmetrical)
$\mu = 0$

60. No. of electrons in $NO_3^- = 7 + 24 + 1 = 32$

No. of electrons in $CO_3^{2-} = 6 + 24 + 2 = 32$

Hence they are isoelectric. Further

Total no. of valence electrons in NO_3^-

$= 5 + 6 \times 3 + 1 = 24$

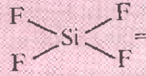
Total no. of valence electrons in CO_3^{2-}

$= 4 + 6 \times 3 + 2 = 24$

∴ Hybridization of central atom in both cases is sp^2. Hence they are isostructural also.

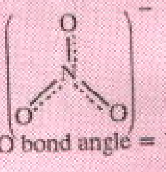
61. Bond energy of sigma bond is greater than that for pi-bond (For C—C sigma bond, it is = 347 kJ mol^{-1} and for π-bond, it is = 264 kJ mol^{-1}).

62. All of them are triangular planar with a bond angle of 120°.

63. μ for O = C = O and  = 0

NO_2 and O_3 are bent molecules with permanent dipole moment.

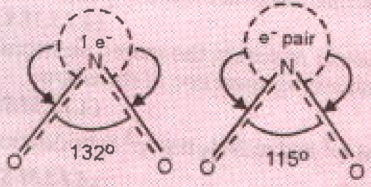
64. O_2F_2 and H_2O_2 both have open book type structure (see page 6/47). They however differ in bond angles and bond lengths.

65. NO_3^- has sp^2 hybridisation and three resonating structures 

Hence ONO bond angle = 120°

NO_2^+ has no unshared electron and *sp* hybridisation. Hence shape is linear ($\ddot{O} = \overset{+}{N} = \ddot{O}$) with bond angle = 180°

NO_2 has one unshared electron whereas NO_2^- has one unshared electron pair. Hence in NO_2^-, the repulsion on the bond pairs are more and angle is less



66. Dipole moment of acetophenone is 3 Debye which is the maximum among the given compounds.

67. See Fig. 6.49 page 6/53, 54.

B.pt. : $NH_3 > AsH_3 > PH_3$

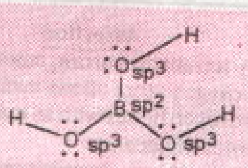
68. Greater the effective nuclear charge, greater is the pull on the electron by the nucleus, smaller is the radius.

69. Similar to ClF_3, discussed on page 6/44.

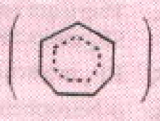
70.

H_2S	<	NH_3	<	SiH_4	<	BF_3
92·6°		107°		109° 28′		120°

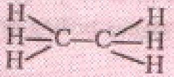
71.



72. I. $H_2C = CH_2$ II. $HC \equiv CH$ III.



IV.



Multiplicity of bond (or bond order

I = 2, II = 3, III = $1\frac{1}{2}$, IV = 1

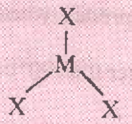
Greater the multiplicity (bond order), less is the bond length.

73. Refer to Q. 65.

74. *sp* hybridized orbital is smallest in size. Hence *sp*-hybridized carbon has highest electronegativity.

75. H — O — O bond angle on H_2O_2 is nearly 97°.

76.



, $\mu = 0$. Hybridization of M = sp^2

77. HF is least volatile due to strong hydrogen bonding.

78. In NH_3, octet of N is complete. Hence it is not electron deficient.

ADDITIONAL QUESTIONS

For All Competitive Examinations

Assertion-Reason Type Questions

The questions given below consist of an 'Assertion' in column 1 and the 'Reason' in column 2. 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 the reason is INCORRECT.

(*d*) If both assertion and reason are INCORRECT.

	Assertion	Reason
1.	If the central atom in a molecule is surrounded only by shared pairs of electrons, the molecule has a regular geometry.	The shared pairs of electrons repel each other with equal force so that all bonds are equidistant from each other.
2.	When two noble gas atoms are brought very close together, their surrounding electron-clouds influence each other, and a force of attraction is built up between them.	The random variation in the positions of electrons around one nucleus may create a transient electric dipole, which induces a transient, opposite dipole in the nearby atoms.

Assertion	Reason
3. The nearly tetrahedral arrangement of the orbitals about the oxygen atom allows each water molecule to form hydrogen bonds with as many as four neighbouring water molecules.	In ice, each water molecule forms four hydrogen bonds as each molecule is fixed in space.
4. There are ten valence electrons on sulphur atom in SF_4 molecule.	The structure of SF_4 molecule is a distorted trigonal bipyramid.
5. BF_3 molecule is planar while NF_3 is pyramidal.	N atom is smaller than B.
6. *o*-Nitrophenol has a higher boiling point than *p*-Nitrophenol.	Intramolecular hydrogen bonding occurs in *p*-Nitrophenol.
7. Ionic compounds tend to be non-volatile.	The intermolecular forces in these compounds are weak. *(A.I.I.M.S. 1994)*
8. The atoms in a covalent molecule are said to share electrons, yet some covalent molecules are polar.	In a polar covalent molecule, the shared electrons spend more time than average near one of the atoms. *(A.I.I.M.S. 1996)*
9. NO_3^- is plannar while NH_3 is pyramidal.	N in NO_3^- has sp^2 and in NH_3 has sp^3 hybridization. *(A.I.I.M.S. 1997)*
10. The bond angle of PBr_3 is greater than that of PH_3 but bond angle of NBr_3 is less than that of NH_3.	Electronegativity of phosphorus atom is less than that of nitrogen. *(A.I.I.M.S. 1998)*
11. The dipole moment helps to predict whether a molecule is polar or non-polar.	The dipole moment helps to predict the geometry of molecules. *(A.I.I.M.S. 1999)*
12. All F–S–F angles in SF_4 are greater than 90° but less than 180°.	The lone pair-lone pair repulsion is weaker than bond pair-bond pair repulsion. *(A.I.I.M.S. 2004)*

True/False Statements

Select the true and false statements from the following statements :

1. A group of atoms having characteristic properties is known as a molecule.
2. The term chemical bond dos not express the existence of strong forces of attraction between the atoms.
3. The attractive force responsible for molecule formation is the electrical force between electrons and nuclei. However, not all electrons in an atom are involved in molecule formation.
4. Lewis symbols do not show inner shell electrons.
5. The most obvious way for an atom to have an octet in its valence shell is to acquire additional electrons if it has less than eight valence electrons or to lose all its outer electrons.
6. Many physical and chemcial properties are the result of the shape that a molecule has.
7. The direction of the bonds around an atom in a molecule does not depend on the total number of electron pairs (bonding as well as non-bonding) in the valence shell of the atom.
8. Ionic bond is not an extreme case of a covalent bond.
9. Molecule of H_2O is angular in shape.
10. Molecule of methane is tetrahedral.
11. The presence of polar bonds in a polyatomic molecule suggests that the molecule has non-zero dipole moment. *(I.I.T. 1990)*

Fill In The Blanks

1. According to electronic theory, atoms combine with each other to complete their..........
2. An ionic bond is formed by .... of electrons.
3. A covalent bond is formed by .... of electrons.
4. For an ionic bond to be formed between two atoms, the metal atom should have .... ionization energy and non-metal atom should have .... electron affinity.
5. Ionic compounds are .... in water and have .... melting points.
6. A double bond implies......shared pair of electrons.
7. The two atomic orbitals that overlap to form a bond must have .... electron/electrons each.
8. The two electrons that occupy a bonding orbital must have ....
9. The structures represented by electron dots are called ....

10. When overlapping of half-filled atomic orbitals takes place along the internuclear axis, the bond formed is called .... bond. If it takes place sideways, the bond formed is called .... bond.

11. Sigma bond is .... than pi bond.

12. Electronegativity is the power to attract.......electrons.

13. Electronegativity of .... is maximum and is zero for ....

14. A covalent bond formed is non-polar if the two atoms have .... electronegativity.

15. A bond is said to be ionic if the electronegativity difference between two atoms is greater than ....

16. Dipole moment of a diatomic polar molecule is the product of ....

17. Mixing of orbitals of a shell to form equivalent orbitals is called ....

18. When $2s^1$, $2p_x^1$ and $2p_y^1$ orbitals mix to for three new equivalent orbitals, it is called .... hybridisation.

19. The hybridisation involved in BeF_2 is .... The shape is .... The bond angle is ....

20. The hybridisation involved in BF_3 is .... The shape is .... The bond angle is ....

21. A double bond is always made of a .... bond and a .... bond.

22. A co-ordinate bond is formed by.........of electrons.

23. For hydrogen bonding to occur, hydrogen atom must be linked to .... atom.

24. The boiling point of water is .... than that of H_2S because of ....

25. HF has .... boiling point than HCl because of ....

26. The density of ice is .... than that of water due to the formation of ....

27. The atom which loses electrons acquires a .... charge.

28. Hydrogen bond energy is around............ *(Roorkee 1989)*

29. The hybridisation state of oxygen in water molecule is .... *(Roorkee 1990)*

30. The valence atomic orbitals on carbon in silver acetylide is .... hybridized. *(I.I.T. 1990)*

31. Greater stability of an ionic compound indicates .... lattice energy.

32. Among N_2O, SO_2, I_3^+ and I_3^-, the linear species are .... and .... *(I.I.T. 1997)*

Matching Type Questions

Match items in column A with items in column B.

Column A	**Column B**
(*i*) Methane molecules	(*a*) covalency
(*ii*) Sharing of electrons	(*b*) tetrahedral molecule
(*iii*) H_2O	(*c*) pyramidal molecule
(*iv*) NH_3	(*d*) zero dipole moment
(*v*) BeF_2	(*e*) polar molecule.
(*vi*) BF_3 molecule	(*f*) linear molecule.

ANSWERS

ASSERTION-REASON TYPE QUESTIONS

1. *a* **2.** *a* **3.** *b* **4.** *b* **5.** *b* **6.** *d* **7.** *c* **8.** *c* **9.** *a* **10.** *b* **11.** *a* **12.** *c*

TRUE/FALSE STATEMENTS

1. True **2.** False **3.** True **4.** True **5.** True **6.** True **7.** False **8.** False **9.** True **10.** True **11.** False.

FILL IN THE BLANKS

1. octets **2.** transference **3.** mutual sharing **4.** low, high **5.** soluble, high **6.** two **7.** one **8.** opposite spin **9.** Lewis structures **10.** sigma, pi **11.** stronger **12.** shared pairs **13.** F, noble gases **14.** same **15.** 1.9 **16.** charge, internuclear distance **17.** hybridisation **18.** sp^3 **19.** *sp*, linear 180° **20.** sp^2 triangular planar, 120° **21.** sigma, pi **22.** one sided sharing **23.** a highly electronegative **24.** higher, hydrogen bonding **25.** higher, hydrogen bonding **26.** less, a cage like structure (open structure) **27.** positive **28.** 4.2—8.4 kJ mol^{-1} **29.** sp^3 **30.** *sp* **31.** large negative. **32.** N_2O and I_3^-

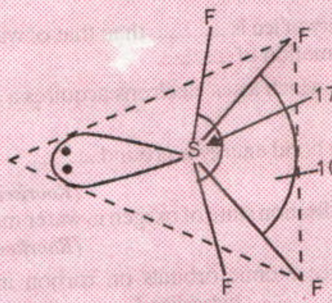
MATCHING TYPE QUESTIONS

(*i*)— (*b*), (*ii*)— (*a*), (*iii*)— (*e*), (iv)— (*c*), (*v*)— (*b*), (*vi*)— (*d*).

HINTS/EXPLANATIONS to Assertion-Reason Type Questions

4. $_{16}S$ = 2, 8, 6. It has 6 valence electrons. Four of these are shared with 4 F atoms. Hence total valence electrons in SF_4 = 6 + 4 = 10.

(sp^3d hybridisation, lone pair repels the bond pairs)



5. N atom is smaller than B because along a period atomic size decreases but this is not the explanation for planar shape of BF_3 and pyramidal shape of NF_3.

6. o-Nitrophenol has lower boiling point than *p*-Nitrophenol due to intermolecular H-bonding in the former.

7. Intermolecular forces in ionic compounds are strong.

8. The shared pair remains attracted towards the more electronegative atom at all times.

10. The truth of assertion is not due to difference in the electronegativities of N and P but due to difference in electronegativity of H and Br (in NH_3 and NBr_3) and due to resonance in PBr_3 but no resonance in PH_3 (See page 6/69).

12. Due to greater lone pair - bond pair repulsion than bond pair- bond pair repulsions, the F—S—F bond angle decreases from 180°.