

### What is Nuclear Transmutation ?

Nuclear transmutation, in general, may by defined as the conversion of one element into another, *i.e.*, one type of atom into another. Nuclear transmutation is such a conversion achieved by artificial means, as distinct from the spontaneous transmutation witnessed in natural radioactive substances. Nuclear transmutation is also called **nuclear transformation** or **disintegration** or **nuclear reaction**, since the transmuted element disintegrates forming a different new element.

The study of the natural radioactive phenomena paved the way for artificial transmutation. For, the occurrence of spontaneous disintegration of the nucleus in the heavy radioactive elements readily suggested the idea whether it might not be possible to break up nuclei of other ordinarily stable elements by bombarding them artificially with high-speed particles Rutherford took up the hint and performed a series of experiments in which the atoms of different stable elements such as nitrogen, aluminium, phosphorus, etc., were subjected to an intense bombardment by the high velocity  $\alpha$ -particles (as *projectiles*) obtained from natural radioactive substances and finally, in 1919, succeeded in transmuting these elements. Now a days other bombarding particles (*i.e.*, projectiles) like protons

 $\binom{1}{1}H$ , deuterons  $\binom{2}{1}H$  etc., are also used for the same purpose.

Rutherford, in his first experiment which he performed to demonstrate the first artificial transmutation, directed a beam of  $\alpha$ -particles obtained from radium against a thin layer of nitrogen. The outcoming  $\alpha$ -particles were then absorbed by placing some material (e.g. 1 mm thick aluminium foil) in between the nitrogen and ZnS screen. This indicated the presence of some new particles, which were identified from their deflection in the magnetic field as high energy protons  $(\frac{1}{1}H)$ . The capture of an  $\alpha$ -particle followed by the ejection of a proton led Rutherford to believe that  $\frac{14}{7}N$  is transformed into a rare isotope of oxygen,  $\frac{17}{8}O$ . This transformation (or disintegration or nuclear reaction as it is called) may be represented by an equation similar to that used for chemical reactions :

Since, like chemical equations, such equations must balance the charge and mass numbers have to be the same on the two sides of these equations.

The above reaction may also be represented by the abbreviated notation : <sup>14</sup>N  $(\alpha, p)$  <sup>17</sup>O which would be interpreted as follows : when a nitrogen (<sup>14</sup>N) nucleus, called *target nucleus*, interacts with an alpha particle ( $\alpha$ ), referred to as *incident* or *projectile* (*bombarding particle* or *bullet*), a proton (p) is ejected and an oxygen (<sup>17</sup>O) nucleus called *recoil* nucleus remains behind.

The exact nature of the nuclear reaction which takes place when an  $\alpha$ -particle makes head-on collision with a nitrogen nucleus was not clearly understood at first. However, soon a satisfactory explanation backed by experimental verification was achieved. It was proved that  $\alpha$ -particle is captured by nitrogen nucleus thus forming an *unstable compound nucleus (fluorine atom, not found in nature)* which immediately disintegrates by ejecting a proton (<sup>1</sup><sub>1</sub>H). The intermediate unstable nucleus is shown in bracket.

 $\begin{array}{cccc} {}^{14}_{7}\mathrm{N} + {}^{4}_{2}\mathrm{He} & \rightarrow & [{}^{18}_{9}\mathrm{F}] & \rightarrow & {}^{17}_{8}\mathrm{O} + {}^{1}_{1}\mathrm{H} \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ \end{array} \right) \rightarrow & {}^{17}_{8}\mathrm{O} + {}^{1}_{1}\mathrm{H} \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ \end{array} \right) \rightarrow & {}^{17}_{8}\mathrm{O} + {}^{1}_{1}\mathrm{H} \\ & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ \end{array}$ 

Hence, it is seen that starting with two stable nuclei of helium and nitrogen, we get two stable nuclei of oxygen and hydrogen. In other words, an atom of nitrogen has been transformed into an atom of oxygen. This process is called **transmutation of elements.** Since the intermediate compound molecule has temporary existence, its is often omitted from any discussion of the nuclear reaction.

The  ${}^{17}_{8}$ O nucleus formed in this nuclear reaction is stable and hence this nuclear reaction does not lead to the production of artificial radioactivity.

Rutherford, encouraged by this first success, continued his researches and in collaboration with Chadwick (1921 – 24) showed that many other light elements, from boron (Atomic No. 5) to potassium (Atomic No. 19) with the exception of carbon and oxygen, could be transmuted by bombardment with  $\alpha$ -particles, resulting in the emission of protons (<sup>1</sup><sub>1</sub>H). Some of these nuclear reactions are given below :

Light elements		α <i>-particles</i>		Intermediate unstable compound nucli			e	Stable elements ie			Protons ( <sup>1</sup> <sub>1</sub> H)	
	<sup>10</sup> <sub>5</sub> B	+	<sup>4</sup> <sub>2</sub> He	3.	$\rightarrow$	[ <sup>1</sup> <sup>4</sup> N]		$\rightarrow$	<sup>13</sup> <sub>6</sub> C	+	łΗ	
hn.	<sup>23</sup> <sub>11</sub> Na	+	<sup>4</sup> <sub>2</sub> He		$\rightarrow$	[ <sup>27</sup> <sub>13</sub> Al]		$\rightarrow$	$^{26}_{12}$ Mg	+	1H	
	<sup>27</sup> <sub>13</sub> Al	+181	<sup>4</sup> <sub>2</sub> He		$\rightarrow$	[ <sup>31</sup> <sub>15</sub> P]	- 5-	$\rightarrow$	$^{30}_{14}{ m Si}$	+	1H	
	$^{32}_{16}{ m S}$	+ 1	<sup>4</sup> <sub>2</sub> He		$\rightarrow$	[ <sup>36</sup> <sub>18</sub> Ar]	111	$\rightarrow$	35 17Cl	+	łΗ	
	$^{39}_{19}{ m K}$	+	${}_{2}^{4}\text{He}$		$\rightarrow$	[ <sup>43</sup> <sub>21</sub> Sc]	21	->	<sup>42</sup> <sub>20</sub> Ca	+	lΉ	

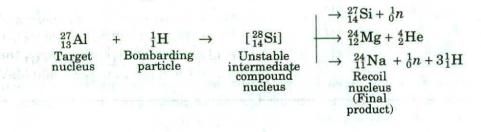
It will be seen that in each case, charge of the product nucleus is increased by one unit and the mass is increased by three units. Such reactions are also referred to as  $(\alpha, p)$  reactions. A serious difficulty that arose during these transmutation reactions was that the yield of protons produced rapidly decreased with increasing atomic number of the target nuclei. This was due to that fact the  $\alpha$ -particles, being positively charged, are repelled by the positive charge on the target nuclei. Thus  $\alpha$ -particles are deflected away or scattered as they approach the positive field of the target nucleus. Consequently,  $\alpha$ -particles are not focused properly on to the target nuclei. This indicated that  $\alpha$ -particles did not have sufficient energy to penetrate the target nucleus. Hence, attention was directed towards exploring the means to obtain high-velocity charged particles from suitable high-voltage accelerators. In 1932, Cockcroft and Walton, working in Rutherford's laboratory, constructed the first high tension machine (atom smascher) which could accelerate protons to one million electron volts. Using the artificially accelerated protons of energy 0.15 MeV they brought about the transmutation of  $\frac{7}{3}$ Li. This was the first case of a nuclear disintegration brought about by purely artificial means.

 ${}^{7}_{3}\text{Li} + {}^{1}_{1}\text{H} \rightarrow [{}^{8}_{4}\text{Be}] \rightarrow {}^{4}_{2}\text{He} + {}^{4}_{2}\text{He}(p, 2\alpha)$ Unstable
nucleus

As shown in the nuclear equation given above, a portion of energy 0.15 MeV enters a lithium nucleus to form a new but unstable beryllium nucleus. This nucleus splits up into two  $\alpha$ -particles which are driven apart with great violence. The production of  $\alpha$ -particles in the above nuclear reaction was confirmed by following their track in cloud chambers. Meanwhile, E.O. Lawrence and co-workers, at the University of California, devised an instrument called **cyclotron** for the purpose. A modified instrument called **synchroton** has been built and designed to produce the protons of ten billion electron volts energy.

#### **Bohr's Theory of Nuclear Reactions**

According to Bohr's theory, the bombarding particle combines with the target nucleus to form an intermediate compound nucleus which is in the excited state and hence is unstable. This unstable intermediate compound nucleus has small life period  $(10^{-12} \text{ to } 10^{-14} \text{ seconds})$  and hence breaks up to give the final product, called recoil nucleus. The nature of the final product depends on the amount of energy associated with the unstable intermediate compound nucleus. For example when  $^{27}_{13}$ Al is bombarded with protons  $(^{1}_{1}\text{H})$ , an unstable intermediate compound nucleus,  $[^{28}_{14}\text{Si}]$  is formed which breaks up in any of the following ways depending on the amount of energy associated with the intermediate compound nucleus.



#### **Classification of Nuclear Reactions**

The classification of nuclear reactions can be made (1) on the basis of overall energy transformation that occurs during the nuclear reaction, and (2) on the basis of the nature of the bombarding particle used to bombard the target nucleus. Thus the following two classifications are obtained :

I. Classification based on overall energy transformation. This classification gives the following types of nuclear reactions :

(1) Capture reactions. In these reactions the bombarding particle is captured or absorbed by the target nucleus with the emission of  $\gamma$ -rays. For example :

 ${}^{85}_{37}\text{Rb} + {}^{1}_{0}n \rightarrow {}^{86}_{37}\text{Rb} + {}^{0}_{0}\gamma$   ${}^{12}_{6}\text{C} + {}^{1}_{1}\text{H} \rightarrow {}^{13}_{7}\text{N} + {}^{0}_{0}\gamma$   ${}^{238}_{92}\text{U} + {}^{1}_{0}n \rightarrow {}^{239}_{92}\text{U} + {}^{0}_{0}\gamma$ 

(2) Particle-particle reactions. In these reactions the bombarding particle is absorbed by the target nucleus to form the compound nucleus which breaks down to give the final product. For example :

$^{24}_{11}\text{Na} + {}^{4}_{2}\text{He} \rightarrow$	$\left( \right) \rightarrow \frac{26}{13} \text{Al} + 2\frac{1}{0}n$
$^{27}_{13}\text{Al} + ^{1}_{0}n \rightarrow$	$28_{A1} \rightarrow \frac{28}{13} \text{Al} + \frac{0}{9} \gamma$
$^{26}_{12}Mg + ^{2}_{1}H \rightarrow$	$\begin{vmatrix} 13^{\text{AI}} \\ \rightarrow \frac{27}{12}\text{Mg} + \frac{1}{1}\text{H} \end{vmatrix}$
$^{27}_{12}Mg + {}^{1}_{1}H \rightarrow$	$\left( \right) \rightarrow \frac{24}{11}\text{Na} + \frac{4}{1}\text{He}$
	Compound nucleus

(3) Fission reactions. These are the reactions in which a heavier nucleus breaks down into two or more lighter nuclei of almost equal size and a large amount of energy is also liberated. For example  $^{235}_{92}$ U breaks down into  $^{144}_{56}$ Ba and  $^{90}_{36}$ Kr nuclei by slow neutrons.

 $^{235}_{92}$ U +  $^{1}_{0}n$  (slow)  $\rightarrow ^{144}_{56}$ Ba +  $^{90}_{36}$ Kr +  $2^{1}_{0}n$  + Energy

(4) Fusion reactions. These are the reactions in which two lighter nuclei are combined or fused together to give a stable and heavier nucleus, and a large amount of energy is liberated. For example the fusion or combination of deuterium  $\binom{2}{1}$ H) and tritium  $\binom{3}{1}$ H) gives a stable nucleus of helium  $\binom{4}{2}$ He) and energy equal to 17.6 MeV is also liberated.

 $^{2}_{1}\text{H} + ^{3}_{1}\text{H} \rightarrow ^{4}_{2}\text{He} + ^{1}_{0}n + 17.6 \text{ MeV} \rightarrow$ 

(5) Spallation reactions. These reactions were discovered by Seaborg and Perimen in 1947. In these reactions the high-speed bombarding particle is absorbed to form a normal nucleus and a large number of light particles. For example, the bombardment of  $^{63}_{29}$ Cu nucleus by high-speed  $\alpha$ -particle having energy = 400 MeV gives  $^{37}_{17}$ Cl nucleus 14 protons and 16 neutrons.

$$^{63}_{29}$$
Cu +  $^{4}_{2}$ He  $\rightarrow ^{37}_{17}$ Cl + 14  $^{1}_{1}$ H + 16  $^{1}_{0}$ n.

**II. Classification based on the nature of the bombarding particle.** This classification gives the following types of nuclear reactions :

(1) Nuclear reactions induced by alpha particles  $({}_{2}^{4}He)$ . These reactions may be of following types :

(a)  $(\alpha, p)$  reactions. These reactions are common with the elements of low atomic number. Examples are :

(b)  $(\alpha, n)$  reactions. By using more energetic  $\alpha$ -paticles these reactions may be obtained. Examples are :

$${}^{9}_{4}\text{Be} + {}^{4}_{2}\text{He} \rightarrow {}^{12}_{6}\text{C} + {}^{1}_{0}n$$

$${}^{40}_{18}\text{Ar} + {}^{4}_{2}\text{He} \rightarrow {}^{43}_{20}\text{Ca} + {}^{1}_{0}n$$

$${}^{7}_{3}\text{Li} + {}^{4}_{2}\text{He} \rightarrow {}^{10}_{5}\text{B} + {}^{1}_{0}n$$

(c)  $(\alpha, \gamma)$  reactions. Following is a typical example of this type of reaction.

$${}_{3}^{7}\text{Li} + {}_{3}^{4}\text{He} \rightarrow {}_{5}^{11}\text{B} + {}_{0}^{0}\gamma$$

(2) Nuclear reactions induced by protons  $({}_{1}^{1}H)$ . These reactions are of the following types.

(a)  $(p, \alpha)$  reactions. Examples are :

$$\begin{array}{rcl} {}^{7}_{3}\mathrm{Li}+{}^{1}_{1}\mathrm{H}&\rightarrow&{}^{4}_{2}\mathrm{He}+{}^{4}_{2}\mathrm{He}\\ {}^{19}_{9}\mathrm{F}+{}^{1}_{1}\mathrm{H}&\rightarrow&{}^{16}_{8}\mathrm{O}+{}^{4}_{2}\mathrm{He}\\ {}^{14}_{7}\mathrm{N}+{}^{1}_{1}\mathrm{H}&\rightarrow&{}^{11}_{6}\mathrm{C}+{}^{4}_{2}\mathrm{He}\\ {}^{9}_{4}\mathrm{Be}+{}^{1}_{1}\mathrm{H}&\rightarrow&{}^{6}_{3}\mathrm{Li}+{}^{4}_{2}\mathrm{He} \end{array}$$

(b) (p, n) reactions. If proton has sufficient energy, probability of (p, n) type reactions becomes high. Some examples are :

$${}^{18}_{8}\text{O} + {}^{1}_{1}\text{H} \rightarrow {}^{18}_{9}\text{F} + {}^{1}_{0}n$$

$${}^{58}_{28}\text{Ni} + {}^{1}_{1}\text{H} \rightarrow {}^{58}_{29}\text{Cu} + {}^{1}_{0}n$$

$${}^{65}_{29}\text{Cu} + {}^{1}_{1}\text{H} \rightarrow {}^{65}_{30}\text{Zn} + {}^{1}_{0}n$$

$${}^{23}_{11}\text{Na} + {}^{1}_{1}\text{H} \rightarrow {}^{23}_{12}\text{Mg} + {}^{1}_{0}n$$

(c)  $(p, \gamma)$  reactions. With proton as the projectile, radiative capture processes of  $(p, \gamma)$  type have been observed for a number of lighter elements.

$$\begin{array}{rcl} & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & &$$

$${}^{14}_{7}\mathrm{N} + {}^{1}_{1}\mathrm{H} \rightarrow {}^{15}_{8}\mathrm{O} + \gamma$$

$${}^{50}_{24}\mathrm{Cr} + {}^{1}_{1}\mathrm{H} \rightarrow {}^{51}_{25}\mathrm{Mn} + \gamma$$

(d) (p, D) reactions. These reactions are more common with heavier elements and protons are of fairly high energy.

$${}^{9}_{4}\text{Be} + {}^{1}_{1}\text{H} \rightarrow {}^{8}_{4}\text{Be} + {}^{2}_{1}\text{H} \text{ or } D$$
$${}^{7}_{3}\text{Li} + {}^{1}_{1}\text{H} \rightarrow {}^{6}_{3}\text{Li} + {}^{2}_{1}\text{H} \text{ or } D$$

(3) Nuclear reactions induced by deuterons  $({}_{1}^{2}H \text{ or } D)$ . Some of the nuclear reactions induced by deuterons are given below :

 $\begin{array}{l} \text{(a) (D, \alpha) reactions induced by deuterons are g} \\ (a) (D, \alpha) reactions. \\ & \begin{array}{c} {}^{6}_{3}\text{Li} + {}^{2}_{1}\text{H} \rightarrow {}^{4}_{1}\text{He} + {}^{4}_{2}\text{He} \\ & \begin{array}{c} {}^{6}_{3}\text{Ca} + {}^{2}_{1}\text{H} \rightarrow {}^{4}_{7}\text{N} + {}^{4}_{2}\text{He} \\ & \begin{array}{c} {}^{40}_{20}\text{Ca} + {}^{2}_{1}\text{H} \rightarrow {}^{14}_{7}\text{N} + {}^{4}_{2}\text{He} \\ & \begin{array}{c} {}^{40}_{20}\text{Ca} + {}^{2}_{1}\text{H} \rightarrow {}^{38}_{19}\text{K} + {}^{4}_{2}\text{He} \\ & \begin{array}{c} {}^{40}_{20}\text{Ca} + {}^{2}_{1}\text{H} \rightarrow {}^{38}_{19}\text{K} + {}^{4}_{2}\text{He} \\ & \begin{array}{c} {}^{40}_{20}\text{Ca} + {}^{2}_{1}\text{H} \rightarrow {}^{38}_{19}\text{K} + {}^{4}_{2}\text{He} \\ & \begin{array}{c} {}^{40}_{20}\text{Ca} + {}^{2}_{1}\text{H} \rightarrow {}^{32}_{19}\text{F} + {}^{1}_{1}\text{H} \\ & \begin{array}{c} {}^{21}_{15}\text{P} + {}^{2}_{1}\text{H} \rightarrow {}^{32}_{19}\text{P} + {}^{1}_{1}\text{H} \\ & \begin{array}{c} {}^{21}_{23}\text{R} + {}^{2}_{1}\text{H} \rightarrow {}^{21}_{11}\text{Na} + {}^{1}_{1}\text{H} \\ & \begin{array}{c} {}^{21}_{6}\text{C} + {}^{2}_{1}\text{H} \rightarrow {}^{13}_{7}\text{N} + {}^{1}_{0}\text{n} \\ & \begin{array}{c} {}^{30}_{52}\text{Te} + {}^{2}_{1}\text{H} \rightarrow {}^{133}_{1}\text{I} + {}^{1}_{0}\text{n} \\ & \begin{array}{c} {}^{209}_{83}\text{Bi} + {}^{2}_{1}\text{H} \rightarrow {}^{210}_{84}\text{Po} + {}^{1}_{0}\text{n} \\ & \begin{array}{c} {}^{21}_{1}\text{H} + {}^{2}_{1}\text{H} \rightarrow {}^{4}_{2}\text{H} + {}^{1}_{0}\text{n} \end{array} \end{array} \end{array} \end{array}$ 

(d) (D, T) reactions.

 $\begin{array}{rcl} {}^{7}_{3}\text{Li} + {}^{2}_{1}\text{H} & \rightarrow & {}^{6}_{3}\text{Li} + {}^{3}_{1}\text{T} \mbox{ (or } {}^{3}_{1}\text{H}) \\ {}^{109}_{47}\text{Ag} + {}^{2}_{1}\text{H} & \rightarrow & {}^{108}_{47}\text{Ag} + {}^{3}_{1}\text{T} \\ {}^{31}_{15}\text{P} + {}^{2}_{1}\text{H} & \rightarrow & {}^{315}_{15}\text{P} + {}^{3}_{1}\text{T} \end{array}$ 

(4) Nuclear reactions induced by neutrons  $({}_{0}^{1}n)$ . In these reactions the neutrons are captured resulting in the emission of any of the following : (a)  $\gamma$ -rays (b)  $\alpha$ -particle (c) proton (d) neutron. Thus these reactions may be of the following types :

(a)  $(n, \gamma)$  reactions. Examples are given below :

$^{27}_{13}\text{Al} + ^{1}_{0}\text{n}$	$\rightarrow$	$^{28}_{13}\text{Al} + ^{0}_{0}\gamma$
$^{115}_{49}$ In + $^{1}_{0}$ n	$\rightarrow$	$^{116}_{49}In + {}^{0}_{0}\gamma$
$^{238}_{02}U + ^{1}_{0}n$	$\rightarrow$	$^{239}_{02}U + ^{0}_{0}\gamma$

(b)  $(n, \alpha)$  reactions. Examples are :

(c) (n, p) reactions. In these reactions the final product is a new element whose atomic number is one unit less than the target nucleus and atomic weight is the same. Examples are :

$$\begin{array}{rcl} {}^{24}_{12}\mathrm{Mg} + {}^{1}_{0}\mathrm{n} & \to & {}^{24}_{12}\mathrm{Mg} + {}^{1}_{1}\mathrm{H} + {}^{0}_{-1}\mathrm{e} \\ {}^{14}_{7}\mathrm{N} + {}^{1}_{0}\mathrm{n} & \to & {}^{14}_{7}\mathrm{N} + {}^{1}_{1}\mathrm{H} + {}^{0}_{-1}\mathrm{e} \\ {}^{64}_{30}\mathrm{Zn} + {}^{1}_{0}\mathrm{n} & \to & {}^{64}_{30}\mathrm{Zn} + {}^{1}_{1}\mathrm{H} + {}^{0}_{-1}\mathrm{e} \end{array}$$

Thus we find that the final product is the same as the target nucleus and hence the overall effect is that the bombarding neutron splits up into a proton and an electron.

(d) (n, 2n) reactions. When the kinetic energy of the bombarding neutron is about 10 MeV, it is able to eject two neutrons from nucleus. For higher energies, more than two neutrons may be ejected. Examples are :

In these cases the product nucleus invariably decays with the emission of a positron. For example :

$$^{38}_{19}\mathrm{K} \rightarrow ~^{38}_{18}\mathrm{Ar} + ~^{0}_{+1}\mathrm{e}_{\mathrm{Positron}}$$

(5) Nuclear reactions induced by tritons  $({}_{1}^{3}H \text{ or }{}_{1}^{3}T)$ . The nuclear reactions induced by tritons are of the following types :

(a) (T, p) reactions

$$^{59}_{27}\text{Co} + ^{3}_{1}\text{H} \rightarrow ~^{61}_{27}\text{Co} + ^{1}_{1}\text{H}$$

(b) (T, d) reactions

$${}^{6}_{3}\text{Li} + {}^{3}_{1}\text{H} \rightarrow {}^{7}_{3}\text{Li} + {}^{2}_{1}\text{H}$$
$${}^{3}_{3}\text{Cu} + {}^{3}_{1}\text{H} \rightarrow {}^{61}_{3}\text{Cu} + {}^{2}_{1}\text{H}$$

$$29$$
Cu +  $1$ H  $\rightarrow 29$ Cu +

(c) (T, n) reactions

$$^{32}_{16}S + ^{3}_{1}H \rightarrow ^{34}_{17}Cl + ^{1}_{0}n$$

(d)  $(T, \alpha)$  reactions

 $^{7}_{3}\text{Li} + ^{3}_{1}\text{H} \rightarrow ^{6}_{2}\text{He} + ^{4}_{2}\text{He}$ 

(6) Nuclear reactions induced by photons or  $\gamma$ -rays  $\begin{pmatrix} 0 \\ 0 \end{pmatrix}\gamma$ . The nuclear reactions induced by photons are called *photo disintegration*. The type of nuclear reactions induced by photons depends on the energy of the incident photon. Various types of reactions produced by photons are given below :

(a)  $(\gamma, n)$  reactions

 ${}^{2}_{1}H + {}^{0}_{0}\gamma \rightarrow {}^{1}_{1}H + {}^{1}_{0}n$   ${}^{9}_{4}Be + {}^{0}_{0}\gamma \rightarrow {}^{8}_{4}Be + {}^{1}_{0}n$   ${}^{31}_{15}P + {}^{0}_{0}\gamma \rightarrow {}^{30}_{15}P + {}^{1}_{0}n$ 

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(b)  $(\gamma, p)$  reactions  ${}^{25}_{12}\mathrm{Mg} + {}^{0}_{0}\gamma \rightarrow {}^{24}_{11}\mathrm{Na} + {}^{1}_{1}\mathrm{H}$ 

(c)  $(\gamma, 2p, n)$  reactions

 $^{27}_{13}\text{Al} + ^{0}_{0}\gamma \rightarrow ~^{24}_{11}\text{Na} + 2^{1}_{1}\text{H} + ^{1}_{0}\text{n}$ 

#### **Nuclear Reactions Vs Chemical Reactions**

Nuclear reactions differ from chemical reactions in the following respects :

(i) In chemical reactions rearrangement of outermost electrons of the atom takes place while the nuclei remain uneffected. Thus no change occurs in the atomic species taking part in the chemical reaction. In other words, no new atomic species are formed in chemical reaction. On the other hand, in nuclear reactions, changes in the number of nucleons present in the nucleus take place and consequently there is formation of new atomic species. Thus nuclear reactions bring about the atomic transmutation or transformation.

(ii) The amount of energy released in nuclear reactions is million times greater than that produced in chemical reactions. This is because of the fact that, in nuclear reaction, unlike in a chemical reaction, a small but measurable loss in mass takes place. This loss in mass is converted into energy, called nuclear reaction energy, in accordance with Eienstein's mass-energy relationship,  $E = mc^2$  where m = loss in mass, E = energy and c = velocity of light.

#### Mass Defect and Binding Energy of the Nucleus

It has been observed that the experimental value of atomic mass (A) of an isotope of an element is invariably less than the sum (M) of the masses of protons, neutrons (called nucleons) and electrons present in the atom of the element. The difference between the two masses is called **mass defect** and is denoted by  $\Delta m$ . Thus :

Mass defect (\Deltam) = Sum of the masses of protons, neutrons and electrons (M)—Experimental value of atomic mass of the isotope (A)

 $\Delta m = \mathbf{M} - \mathbf{A}$ 

or

When the nucleons are allowed to combine together to form the nucleus, some mass disappears in the form of energy, *i.e.* in the combination of nucleons to form the nucleus, some amount of energy is released. The energy released in the formation of a nucleus from its constituent nucleons is called **binding energy of the nucleus**. Conversely, the same amount of energy will naturally be required to break the nucleus into its component nucleons.

If  $\Delta m$  is the mass defect in amu, then binding energy of the nucleus in MeV is equal to  $\Delta m \times 931$  MeV, since 1 amu = 931 MeV of energy. The greater the mass defect, the greater is the binding energy of the nucleus. The binding energy of a nucleus divided by the total number of nucleons (*i.e.* neutrons + protons) is called the binding energy per nucleon in the atom, *i.e.* 

Binding energy per nucleon =	<b>Binding energy</b>	$\Delta m \times 931$ MeV
Binding energy per nucleon =	Neutrons + Protons	A

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The binding energy per nucleon is a measure of the stability of the nucleus. The greater the binding energy per nucleon, greater is the stability associated with the nucleus, *i.e.* the greater the amount of binding energy per nucleon, greater is the force holding the nucleons in the nucleus together.

#### **Calculation of Binding Energy**

How the binding energy of a given nucleus can be calculated can be learnt from the following solved examples :

**Example 1.** Calculate the binding energy of lithium nucleus  $(_{3}Li^{7})$ , given that :

mass	of proton	=	1.00814 amu
mass	of neutron	=	1.00893 amu
			and the second sec

mass of lithium nucleus = 7.01822 amu (A.M.I.E. Summer 1978)

**Solution.** Obviously, the lithium isotope considered is  ${}_{3}\text{Li}^{7}$ . It contains 3 protons and (7 - 3) = 4 neutrons.

Mass of 3 protons $= 3 \times 1.00814 = 3.02442$  amuMass of 4 neutrons $= 4 \times 1.00893 = 4.03572$  amuTotal mass of 7 nucleons,M = 7.06014 amuMass of the lithium nucleus,A = 7.01822 amuMass defect, $\Delta m = M - A = 7.06014 - 7.01822$ 

= 0.04192 amu

 $\therefore$  Binding energy = 931 × 0.04192 = 39 MeV

**Example 2.** The mass of  $_{17}Cl^{35}$  is 34.9800 amu. Calculate its binding energy. What is the binding energy per nucleon ?

Mass of  $_0n^1 = 1.008665$  amu and  $_1H^1 = 1.007825$  amu.

**Solution.** The given chlorine atom has 17 protons and (35 - 17) = 18 neutrons.

Mass of 17 protons = 17 × 1.007825 = 17.133025 amu

Mass of 18 neutrons = 18 × 1.008665 = 18.155970 amu

Total mass of separate constituents = 35.288995 amu

Mass defect,  $\Delta m = 35.288995 - 34.9800$ 

= 0.308995 amu

Now, 1 amu = 931 MeV

: Binding energy of the nucleus = 931 × 0.308995 = 288 MeV

No. of nucleons (*i.e.* protons and neutrons) = 35

:. Binding energy per nucleon = 288/35 = 8.22 MeV

**Example 3.** Calculate the binding energy of a deuteron nucleus, given that mass of neutron = 1.008665 amu, mass of proton = 1.007825 amu and mass of deuteron nucleus = 2.014103 amu.

**Solution.** Neutron mass,  $_0n^1 = 1008665$  amu Proton mass,  $_1H^1 = 1.007825$  amu

Sum = 2.016490 amu

Deuteron mass,	$_{1}H^{2} = 2.014103 \text{ amu}$
Hence	M = 2.014103 amu
and	A = 2.016490 amu
: Mass defect,	$\Delta m = M - A = (2.014103 - 2.016490)$ $= -0.002387$
Binding energy	$= (\Delta m \times 931) \text{ MeV}$
	$= -(0.002387 \times 931) \text{ MeV}$
	= -2.22 MeV

**Example 4.** Calculate the binding energy per nucleon of oxygen atom,  ${}^{16}_{8}O$ , given that mass of  ${}^{16}_{8}O = 15.994910$  amu, mass of neutron = 1.008665 amu, and mass of proton = 1.007277 amu and mass of electron = 0.0005486 amu.

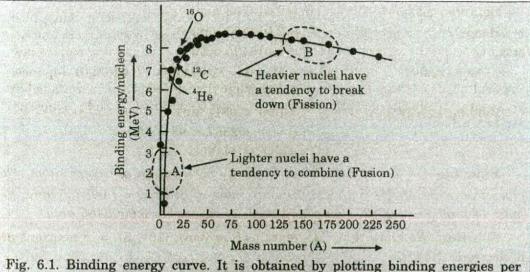
**Solution.** We know that  ${}^{16}_{8}O$  contains 8 protons, (16 - 8) = 8 neutrons and 8 electrons. Now :

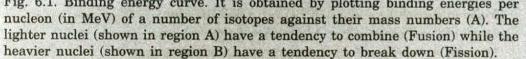
Mass of 8 protons =  $8 \times 1.007277 = 8.058216$  amu Mass of 8 neutrons =  $8 \times 1.008665 = 8.069320$  amu Mass of 8 electrons = 8 × 0.0005486 = 0.0043888 amu Sum, M = 16.1319248 amu Actual mass of oxygen atom, A = 15.994910 amu  $\therefore$  Mass defect,  $\Delta m = M - A$ = (16.1319248 - 15.994910) amu = 0.1370148 amu = 531 MeV of energy, Now, since 1 amu Binding energy of the nucleus  $= (\Delta m \times 931) \text{ MeV}$  $= 0.1370148 \times 931 \text{ MeV}$ = 127.56077 MeVNow, since total number of nucleons = 8 + 8 = 16, Binding energy per nucleon =  $\frac{127.56077}{16}$  MeV = 7.9725 MeV

#### **Binding Energies and Stability of Nuclei**

If the binding energies per nucleon (in MeV) of a number of isotopes are plotted against their mass numbers (A), a graph of the type shown in Fig. 6.1 is obtained. This graph is called *binding energy curve*. The following conclusions may be drawn from this curve.

(i) Lighter nuclei have very small binding energy and hence are unstable. Therefore such nuclei (shown in region A) have tendency to combine or fuse together (*Fusion*) to give the nuclei of intermediate mass number (atomic weight) and higher binding energy or stability. Similarly heavier nuclei are seen to have low binding energy and hence are very unstable. Therefore such nuclei (shown in region B) may break down (*Fission*) to form the nuclei of intermediate atomic weight that possess higher binding energies and greater stability.





(*ii*) The binding energies of some of the light nuclei are very small. The binding energy per nucleon rises sharply and reaches a maximum value of 8.7 MeV in the neighbourhood of a nucleus with mass number, A = 56 (Iron). Thus nucleus of iron is thermodynamically most stable and hence is found in abundance in earth. The graph for the nuclei having mass numbers in the range of 50 to 100 is almost flat. Thus the addition of a single nucleon to any nucleus in the range of A = 50 - 100 increases the binding energy roughly by the same amount. For the nuclei having high mass numbers the value decreases to 7.6 MeV for uranium.

(*iii*) The points for helium (A = 4), carbon (A = 12) and oxygen (A = 16) lie quite high in the graph. Thus the nuclei of these elements are *exceptionally* stable.

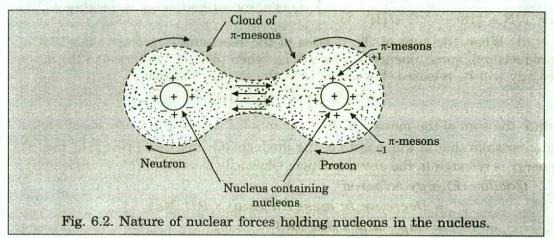
(iv) Over a considerable range of mass numbers, the binding energy per nucleon is 8 MeV which is usually taken as the average value of binding energy for all nucleons.

#### **Meson Theory of Nuclear Forces**

We have already said that the neutrons and protons (*i.e.*, nucleons) are packed together in the nucleus in a very small space, since the nucleus is about  $\frac{1}{10^5}$  in volume as compared to the entire atom. Moreover the protons (positively-charged particles) should ordinarily repell each other, but they are present together in the nucleus. Therefore, a question arises here which is : What is the nature of forces that hold the protons and neutrons together in such a small space? The forces which hold protons and neutrons together in the nucleus are attractive forces and are called **nuclear forces**. These forces are different from electrostatic forces in that the former forces operate only within distances of approximately 0.10 fermi

(=  $10^{-13}$  cm, 1 fermi =  $10^{-12}$  cm) while the latter operate over long range also. Nuclear forces fall rapidly to zero at distances greater than  $14 \times 10^{-13}$  cm and are referred to as *short range forces*. These forces do not obey the inverse square law.

The exact nature of the forces was explained by Hideki Yukawa, a Japanese theoretical physicist, who suggested in 1935 that the nucleons are surrounded by a cloud of negatively-charged and positively-charged  $\pi$ -mesons (\_1 $\pi$  and \_1 $\pi$  mesons) as shown in Fig. 6.2.



These mesons rapidly jump back and forth between the neighbouring nucleons with a velocity approximately equal to that of light. This sort of jumping of mesons keeps the nucleons bound together in the nucleus. Negatively-charged mesons ( $_1\pi$  mesons) interact with protons ( $_{+1}p$ ) while positively-charged mesons ( $_{+1}\pi$  mesons) interact with neutrons ( $_0n$ ) and by these interactions a proton is changed into a neutron and a neutron is changed in a proton. This change takes place for a part of time only.

$${}_{+1}p + {}_{-1}\pi \rightleftharpoons {}_{0}n$$
$${}_{0}n + {}_{+1}\pi \rightleftharpoons {}_{+1}p$$

#### **Q-Value of a Nuclear Reaction**

All types of nuclear reactions are accompained by either the absorption of energy or release of energy. The amount of energy absorbed or released in a nuclear reaction is generally called Q-value of the nuclear reaction. Thus the following two cases arise :

(i) When the sum of the masses of the reactants  $(m_R)$  is less than that of the products  $(m_P)$   $(m_R < m_P)$ , energy is absorbed, *i.e.*, when there is an increase in the mass, energy is absorbed. For example, in the nuclear reaction :

$$^{14}_{7}\text{N} + ^{4}_{2}\text{He} \rightarrow ^{17}_{8}\text{O} + ^{1}_{1}\text{H},$$

since the sum of the masses of the reactants (*i.e.* mass of  ${}^{14}_7\text{N}$  + mass of  ${}^{4}_2\text{He}$ ) is less than that of the masses of the products (*i.e.* mass of  ${}^{17}_8\text{O}$  + mass of  ${}^{1}_1\text{H}$ ), energy is absorbed in this reaction. Obviously Q-value (in MeV) is given by :

# $\begin{array}{l} $Q$-value (Energy absorbed)$\\ $= Increase in mass (in amu) \times 931 \ MeV$\\ $= (m_P - m_R) \times 931 \ MeV$ \end{array}$

Q-value which is absorbed is generally represented by a negative sign. Now if Q-value is incorporated in the above reaction, the reaction can be written as :

 $\left. \begin{array}{c} {}^{14}_{7}\mathrm{N} + {}^{4}_{2}\mathrm{He} + \mathrm{Q} \rightarrow {}^{17}_{8}\mathrm{O} + {}^{1}_{1}\mathrm{H} \\ \mathrm{or} \ {}^{14}_{7}\mathrm{N} + {}^{4}_{2}\mathrm{He} \rightarrow {}^{17}_{8}\mathrm{O} + {}^{1}_{1}\mathrm{H} - \mathrm{Q} \end{array} \right\} \ Q \ is \ absorbed \ and \ hence \ is \ negative$ 

(*ii*) When the sum of the masses of the reactants is greater than that of products  $(m_R > m_P)$ , energy is released, *i.e.* when there is a decrease in the mass, energy will be released. For example in the nuclear reaction :

 ${}^{7}_{3}\text{Li} + {}^{1}_{1}\text{H} \rightarrow {}^{4}_{2}\text{He} + {}^{4}_{2}\text{He},$ 

since the sum of the masses of the reactants (*i.e.* mass of  ${}_{3}^{7}\text{Li}$  + mass of  ${}_{1}^{1}\text{H}$ ) is greater than that of the masses of the products (*i.e.* masses of two  ${}_{2}^{4}\text{He}$  nuclei), energy is released in the above reaction. Obviously Q-value (in MeV) is given by :

Q-value (Energy released) = Decrease in mass (in amu) × 931 MeV = (m<sub>R</sub> - m<sub>P</sub>) × 931 MeV

Q-value which is released is generally represented by a *positive* sign. Now if Q-value is incorporated in the above reaction, the reaction can be written as :

 $\left. \begin{array}{ccc} {}^{7}_{3}\mathrm{Li} + {}^{1}_{1}\mathrm{H} & \rightarrow 2{}^{4}_{2}\mathrm{He} + \mathrm{Q} \\ \mathrm{or} & {}^{7}_{3}\mathrm{Li} + {}^{1}_{1}\mathrm{H} - \mathrm{Q} \rightarrow 2{}^{4}_{2}\mathrm{He} \end{array} \right\} \hspace{0.1cm} Q \hspace{0.1cm} is \hspace{0.1cm} released \hspace{0.1cm} and \hspace{0.1cm} hence \hspace{0.1cm} is \hspace{0.1cm} positive \end{array}$ 

Solved example. Calculate Q-value of the following nuclear reactions

(i)  ${}^{14}_{7}N + {}^{4}_{2}He \rightarrow {}^{17}_{8}O + {}^{1}_{1}H$ 

(ii)  ${}^7_3Li + {}^1_1H \rightarrow 2{}^4_2He$ 

**Solution.** (i)  ${}^{14}_{7}\text{N} + {}^{4}_{2}\text{He} \rightarrow {}^{17}_{8}\text{O} + {}^{1}_{1}\text{H}$ 

The change in mass in atomic-mass-units (amu) can be found as follows :

Interacting particles	<b>Product</b> particles
${}_{2}^{4}\text{He} = 4.00387$	${}^{17}_{8}\mathrm{O} = 17.00450$
${}^{14}_{7}\mathrm{N} = 14.00753$	$^{1}_{1}H = 1.00814$
$Total = 18.01140 = m_R$	$Total = 18.01264 = m_P$
in mass = $(m_P - m_P)$ amu	

Increase in mass =  $(m_P - m_R)$  amu

$$18.01264 - 18.01140 = 0.00124$$
 amu

 $\therefore$  Q-value (Energy absorbed) = 0.00124 × 931 = 1.15 MeV

Since  $m_R < m_P$ , energy is absorbed in this reaction and hence Q-value is negative, *i.e.* Q-value = -1.15 MeV.

(ii)  ${}^{7}_{3}\text{Li} + {}^{1}_{1}\text{H} \rightarrow {}^{4}_{2}\text{He} + {}^{4}_{2}\text{He}$ 

Here, the mass values are as under : Interacting particles Product  ${}^{1}_{1}$ He = 1.00814  ${}^{4}_{2}$ He =  ${}^{7}_{3}$ Li = 7.01822  ${}^{4}_{2}$ He = Total = 8.02636 =  $m_{R}$  Total = Decrease in mass =  $(m_{R} - m_{P})$  amu

 Product particles

  $\frac{4}{2}$ He = 4.00387

  $\frac{4}{2}$ He = 4.00387

 Total = 8.00774 =  $m_P$ 

= 8.02636 - 8.00774 = 0.01862 amu

 $\therefore$  Q-value (Energy released) = 0.01862 × 931 MeV = 17.3 MeV

Since  $m_R > m_P$ , energy is released in this reaction and hence Q-value is positive, *i.e.* Q-value = + 1.73 MeV.

#### **Nuclear Fission**

#### What is Nuclear Fission?

The binding energy curve given in Fig. 6.1 indicates that the heavier nuclei, due to their low binding energies, are unstable and hence break down to produce the nuclei of intermediate atomic weights (*i.e.* mass numbers) that possess higher binding energies and hence greater stability. They do so when they are bombarded with energetic particles such as neutrons. Thus :

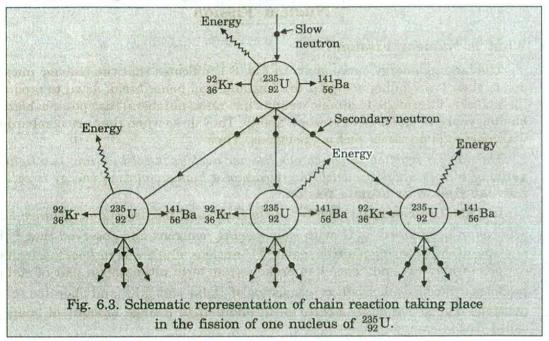
The nuclear reaction in which one heavier nucleus is split up into two lighter nuclei of almost equal size with the release of a huge amount of energy is called **nuclear fission or atomic fission**.

In 1939, German radio chemists, Otto Hahn and his associates, Meitner and Strassman bombarded  $^{235}_{92}$ U with slow moving neutrons and observed that  $^{235}$ U nucleus, after capturing neutron, gave  $^{236}$ U nucleus which was radioactive (called compound nucleus) and hence had broken up to form ultimately a pair of stable products (called fission products) consisting of  $^{141}_{56}$ Ba and  $^{92}_{36}$ Kr and liberated three neutrons (called secondary neutrons) in addition to a huge amount of energy, called fission energy.

 $\overset{235}{_{92}}\text{U} + \overset{1}{_{0}}n \rightarrow \overset{[236}{_{92}}\text{U}] \underset{\text{Compound}}{\overset{\text{Compound}}{_{\text{nucleus}}}} \rightarrow \underbrace{\overset{141}{_{56}}\text{Ba} + \overset{92}{_{36}}\text{Kr}}_{\substack{\text{Pair of stable}\\ \text{products}}} + 3\overset{1}{_{0}}n + \text{Energy} (Fission \ Energy)$ 

Although originally Hahn and Strassman identified by analysis  ${}^{141}_{56}$ Ba and  ${}^{92}_{36}$ Kr as the fission products of  ${}^{235}_{92}$ U, now it is known to split at least in 50 different ways. What particular pair of stable products will be formed *actually depends on chance*. The number of neutrons released depends on the mode of fission and on the energy of the neutrons which have been used to induce the fission. The neutrons are emitted by the fission products and not by the compound nucleus.

In the nuclear fission reaction a huge amount of energy is also liberated. How this energy is produced in a nuclear fission can be explained as follows : Suppose we initiate fission of one  $^{235}$ U nucleus by one neutron obtained either by cosmic rays or by some radioactive source. In this fission process each  $^{235}$ U nuclear suffering fission will liberate three neutrons. These three neutrons will in turn cause the fission of other three  $^{235}$ U nuclei and will liberate three more neutrons in the fission of each  $^{235}$ U nucleus. Thus nine neutrons will be obtained and so on. (*See* Fig. 6.3). Consequently, a self-propagating or self sustaining *chain reaction* (also called *autocatalytic reaction*) starts in which the number of neutrons keeps on multiplying rapidly (in geometrical progression). This chain reaction continues till the whole of  $U^{235}$  has undergone fission. This chain reaction is also accompanied by the liberation of a huge amount of energy which is called **Fission Energy** or **Atomic Energy**. This energy can be either very fast resulting in a violent explosion (as in an atom bomb) or it can be controlled and maintained at a steady rate (as in chain reacting nuclear piles or nuclear reactors).



The amount of energy released in a fission reaction varies from one reaction to another. But, on the average, approximately 200 MeV of energy is released by the fission of one  $U^{235}$  nucleus. This energy (= 200 MeV) is about 500 million times as great as that released per atom in the combination of hydrogen which is the primary heat-producing constituent of coal or oil.

# Calculation of Energy Released in Nuclear Fission : Q-Value of Nuclear Fission

The amount of energy released in a nuclear fission can be calculated by the mass-defect method which is based on the fact that in a nuclear fission reaction, the total mass of the products is always less than that of the reacting nuclei (i.e. parent nuclei). This decrease in mass is called mass defect which is converted into

energy according to mass-energy relationship (Einstein's equation) viz.  $E = mc^2$ . Thus for the nuclear fission of the type :

$$^{235}_{92}\text{U} + ^{1}_{0}\text{n} \rightarrow ^{141}_{56}\text{Ba} + ^{92}_{36}\text{Kr} + 3^{1}_{0}\text{n} + \text{Energy}$$

energy has been calculated to be equal to 250 MeV as shown below :

Interacting particles

 $^{235}_{92}$ U = 235.11750 a.m.u.

 $_{0}^{1}n = 1.00898 \ a.m.u.$ 

 $^{92}_{36}$ Kr = 91.92640 a.m.u.

 $^{141}_{56}Ba = 140.95770 \ a.m.u.$ 

**Product** particles

 $3_0^1 n = 3 \times 1.00898 = 3.02694 \ a.m.u.$ 

Total = 236.12648 amu

Total = 235.91104 amu

: Loss in mass (Mass defect) = 236.12648 - 235.91104

= 0.21544 amu

Therefore, energy released per fission of <sup>235</sup>U nucleus

= 0.21544 × 931 MeV

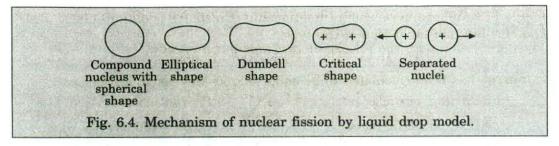
#### = 200.5 MeV.

Out of this energy 170.5 MeV is carried by the fission fragments as kinetic energy, 5 MeV by fission neutrons, 15 MeV by  $\beta$  and  $\gamma$ -rays which are produced due to the radioactivity of the fission fragments and 10 MeV by the neutrons associated with  $\beta$ -decay.

#### Mechanism of Nuclear Fission-Liquid Drop Model of Nuclear Fission

The phenomena of nuclear fission has been explained by liquid drop model suggested by Bohr-Wheeler, since an atomic nucleus has many similarities with a liquid drop. A liquid drop has a spherical shape due to its surface tension. If sufficient energy from outside is applied on the drop to overcome the forces of surface tension, the drop may change it spherical shape to an elliptical shape. If the external energy is sufficiently large, the elliptical shape may change to a dumb-bell shape and ultimately may break into two portions of spherical shape.

As said above, an atomic nucleus has many similarities with a liquid drop and hence behaves as a liquid drop. When sufficient energy is applied on a uranium nucleus through the neutron bombardment, the compound nucleus formed (behaving as a liquid drop) changes its spherical shape to elliptical shape (Fig. 6.4). If the energy applied on the uranium nucleus through the neutron bombardment is sufficiently large, the elliptical shape of the nucleus may change to a dumb-bell shape. Both the parts of the dumb-bell carry positive charge (critical shape). The energy absorbed by the uranium nucleus to change from spherical shape to critical shape is called **threshold energy** required by the fission reaction to occur. Since the two parts of the critical shape have similar (positive) charges, they repell each other and ultimately are separated from each other into two nuclei having the spherical shape and almost the same size.



#### **Uses of Nuclear Fission**

The enormous energy liberated in nuclear fission and the occurrence of chain reaction have been used in *Atomic Bomb (Fission Bomb)* and in *Atomic (or Nuclear)* Pile or Nuclear Reactor.

#### Atomic Bomb (Fission Bomb)

We have already seen that a chain reaction takes place in a nuclear fission reaction and a huge amount of energy is produced. Each  $^{235}$ U nucleus liberates three neutrons (called *secondary neutrons*). Each of these secondary neutrons strikes a fresh  $^{235}$ U nucleus and causes its fission with the liberation of three more secondary neutrons. In reality it has been observed that if the size of  $^{235}$ U nucleus being used for fission is smaller than a minimum size, called **critical size**, some of the secondary neutrons escape into the air and hence no chain reaction takes place to cause explosion and also no vast amount of energy is liberated in an explosive fashion. This size of  $^{235}$ U nucleus which is smaller than the critical size is called **sub-critical size** and is quite safe [See Fig. 6.5 (*a*)] Thus we see that in order that the secondary neutrons do not escape into the air, the size of  $^{235}$ U nucleus should be bigger than the critical size. In this condition a large number of neutrons are captured by  $^{235}$ U nucleus and hence a chain reaction is set up to cause the explosion.

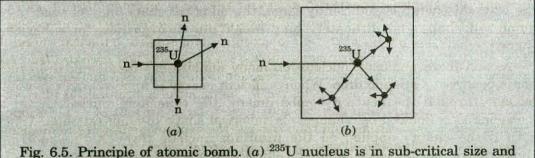
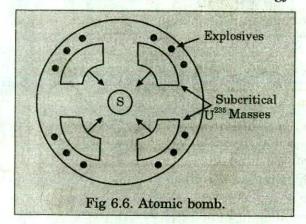


Fig. 6.5. Principle of atomic bomb. (a)  $^{235}$ U nucleus is in sub-critical size and hence no chain reaction takes place to cause the explosion (b)  $^{235}$ U nucleus is in super-critical size and hence chain reaction takes place to cause explosion.

In its safety position an atomic bomb consists of several thousands of pieces of  $^{235}$ U all of which are of sub-critical size. At the time of explosion these are driven together rapidly by firing high explosives like TNT (trinitrotoluene) lying behind each of  $^{235}$ U pieces so that these  $^{235}$ U pieces form one large piece of super-

critical size. Now neutrons from Ra–Be source S (Fig. 6.6) strike the large piece of  $^{235}$ U and a rapid chain reaction is set up. This chain reaction results in a violent explosion with the release of vast amount of energy.



The amount of energy liberated in an atom bomb is equal to that produced by the detonation of about 20,000 tons of TNT. This energy rises the temperature to the order of 10,000,000°C ( $10^7$  °C) and more and produces a pressure of several millions atmosphere. The explosion also produces a violent and intense blast of visible, ultraviolet, X-ray and  $\gamma$ -ray radiations which cause blinding flash.

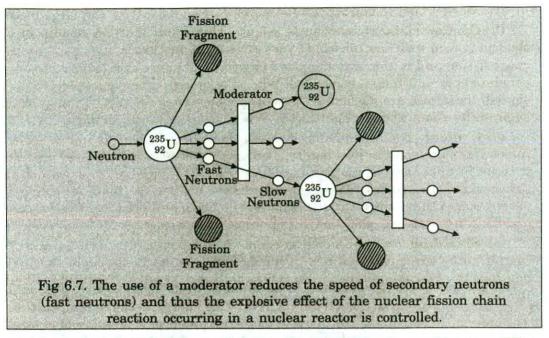
When fission occurs, the fragments fly apart with tremendous speeds. They collide with each other and then kinetic energy is changed into heat energy. The radioactive fragments formed scatter over wide areas and get deposited on the surrounding objects. Thus, we see that in atomic bomb the chain reaction taking place in nuclear fission reaction is *uncontrolled*.

#### **Atomic Pile or Nuclear Reactor**

The study of nuclear reactor can be made under the following headings.

What is a nuclear reactor ? A nuclear reactor is an apparatus in which nuclear fission is produced in the form of a controlled self-sustaining chain reaction. In other words, it is a controlled chain-reacting system supplying nuclear energy. Thus we see that in a nuclear reactor the fission chain reaction is controlled *i.e.* the explosive effect of the nuclear chain reaction taking place in a nuclear reactor is considerably reduced. This is achieved by using natural uranium in place of  $^{235}$ U, since the natural uranium contains a very large amount of  $^{238}$ U isotope which absorbs slow neutrons and thus reduces the explosive effect of the nuclear fission chain reaction seen in case of  $^{235}$ U to a great extent.

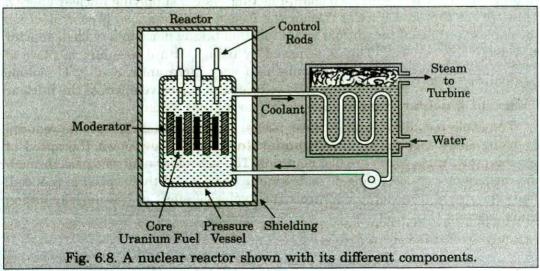
The explosive effect of the nuclear fission chain reaction can also be reduced by using some substances, called **moderators** which slow down the speed of secondary neutrons which are fast neutrons. The secondary neutrons pass through the moderator and lose some of their kinetic energy and their speed is reduced. Thus the use of a moderator controls the explosive effect of the nuclear fission chain reaction (Fig. 6.7).



The materials like  $D_2O$ , graphite etc. have been used as moderators. When graphite is used as a moderator, the reactor is called *Atomic Pile* and when  $D_2O$  is used, it is called *Swimming Pool Reactor*. In atomic pile a huge block of specially purified graphite containing holes in which uranium rods are inserted, acts as moderator. In the swimming pool reactor  $D_2O$  is used in a tank in which the rods of uranium are suspended.

**Components of a nuclear reactor.** The essential components of a nuclear reactor are as follows (Also see Fig. 6.8).

(1) Core. It consists of aluminium plated uranium rods usually 1.5" thick and 4" long in a number of holes. It is this part of a nuclear power plant where fission chain reaction is made to occur and where fission energy is liberated in the form of heat for operating power conversion equipment.



(2) Moderator. It has already been discussed.

(3) Control rods. These are the rods of cadmium or boron steel. These have the ability to absorb neutrons and thus regulate the number of neutrons that can cause fission and in this way the rate of fission and hence the amount of energy generated per unit time is controlled. When the process of nuclear fission is to be slowed, these rods are pushed in. As soon as these rods are raised, the neutrons begin to fly about and the splitting of  $^{235}$ U nucleus grows in intensity.

(4) Coolant. The heat produced in the controlled nuclear fission reaction is removed from the reactor by a liquid called *Coolant*. Since water absorbs neutrons, it is not fit to be used as coolant. In actual practice a liquid alloy of sodium and potassium is used as a coolant. The alloy takes heat to the heat exchanger for raising steam that runs a turbine generator to produce electricity. Heavy water, organic compounds (e.g. polyphenyls), air and  $CO_2$  have also been used as coolants.

(5) Shielding or protective screen. It is an important component of a reactor, although it plays no role in its operation. It stops the heat,  $\gamma$ -rays and neutrons from escaping form the reactor so that they should not be able to harm the persons living in the immediate vicinity. Protective screen is made of special concrete about 8 feet think.

#### Nuclear Fusion

#### What is Nuclear Fusion ?

The binding energy curve given in Fig. 6.1 on page 396 indicates that the lighter nuclei have very small binding energies and hence are unstable. Therefore two or more such nuclei have a tendency to combine or fuse together to give the nucleus of higher mass number (atomic weight) and higher binding energy or stability. Such a nuclear reaction in which two lighter nuclei are combined or fused together to form a heavier (and hence stabler) nucleus is called **nuclear fusion.** In this respect, nuclear fusion is the opposite of nuclear fusion also, large amount of energy is released because the mass of the product nucleus is *less* than the masses of the two nuclei which are fused together. Once fusion reaction is initiated, the energy released is sufficient to maintain the temperature and keep the reaction going on. Nuclear fusion occurs at reasonable rates only at very high temperatures. It is because of this that nuclear fusion reactions are also called *thermonuclear reactions i.e. temperature-dependent reactions*.

#### **Uses of Nuclear Fusion**

Nuclear fusion adequately explains the energy of the solar system, called stellar energy and the basic principle of hydrogen bomb (Fusion bomb).

#### **Stellar Energy**

Stellar energy is the energy of the sun and other stars of the main sequence. Van Weizsacher and Hans Beth (1932) proposed that stellar energy is due to a series of nuclear reactions involving carbon-hydrogen-nitrogen cycle which operates through the following six steps :

#### Modern Inorganic Chemistry

$$\begin{array}{ll} {}^{12}_{6}\mathrm{C} + \frac{1}{1}\mathrm{H} \to {}^{13}_{7}\mathrm{N} + {}^{0}_{0}\gamma + \mathrm{Energy} & \dots(i) \\ {}^{13}_{7}\mathrm{N} & \to {}^{13}_{6}\mathrm{C} + {}^{0}_{1}\mathrm{e} + \mathrm{Energy} & \dots(ii) \\ {}^{13}_{7}\mathrm{N} & \to {}^{13}_{6}\mathrm{C} + {}^{0}_{1}\mathrm{e} + \mathrm{Energy} & \dots(ii) \\ {}^{13}_{6}\mathrm{C} + {}^{1}_{1}\mathrm{H} \to {}^{14}_{7}\mathrm{N} + {}^{0}_{0}\gamma + \mathrm{Energy} & \dots(iii) \\ {}^{14}_{7}\mathrm{N} + {}^{1}_{1}\mathrm{H} \to {}^{15}_{8}\mathrm{O} + {}^{0}_{0}\gamma + \mathrm{Energy} & \dots(iv) \\ {}^{15}_{8}\mathrm{O} & \to {}^{15}_{7}\mathrm{N} + {}^{0}_{1}\mathrm{e} + \mathrm{Energy} & \dots(v) \\ {}^{15}_{7}\mathrm{N} + {}^{1}_{1}\mathrm{H} \to {}^{12}_{6}\mathrm{C} + {}^{4}_{2}\mathrm{He} + \mathrm{Energy} & \dots(vi) \\ \end{array}$$

On adding the nuclear reactions from (i) to (vi) we have :

$$\begin{array}{l} 4\frac{1}{1}H \rightarrow \frac{4}{2}He + 2\frac{0}{1}e + \text{Energy} \\ \text{Proton} & \text{Helium Positron} \end{array} \qquad \dots (1)$$

Nuclear reaction (1) indicates that the stellar energy is produced due to the fusion reaction in which four H-atoms (or protons) are fused together to produce one helium nucleus and two positrons. On the sun the fusion of four H-nuclei into helium nucleus does not take place through a single step but takes place through deuterium  $\binom{2}{1}$ H) as shown below :

$$2^{1}_{1}H \rightarrow {}^{2}_{1}H + {}^{0}_{1}e + \text{Energy} \times 2$$
 ...(*i*)

$$^{2}_{1}H + ^{1}_{1}H \rightarrow ^{3}_{2}He + Energy \times 2$$
 ...(*ii*)

$$2^{3}_{2}\text{He} \rightarrow {}^{4}_{2}\text{He} + 2^{1}_{1}\text{H} + \text{Energy}$$
 ...(*iii*)

On adding :  $4_1^1 H \rightarrow {}_2^4 He + 2_1^0 e + Energy$ 

Energy Released in the Nuclear Fusion of  $4_1^1$ H Nuclei into one \$He and two Positrons ( ${}_1^9$ e).

The amount of energy, Q released in the nuclear fusion reaction,

$$4^{1}_{1}H \rightarrow {}^{4}_{2}He + 2^{0}_{1}e$$

can be calculated by the mass-defect method as shown below (all the masses are given in amu)

$$4^{1}_{1}H \rightarrow {}^{4}_{2}He + 2^{0}_{1}e + Q$$

 $4 \times 1.0084167 = 4.003873 + 2 \times 0.000558 + Q$ 

$$4.0336668 = 4.003873 + 0.001116 + 0.00116 + 0.0$$

or or

...

4.0336668 = 4.004989 + Q

Q = 4.0336668 - 4.004989 = 0.0286778 a.m.u

$$= 0.0286778 \times 931 \text{ MeV} = 26.699032 = 26.7 \text{ MeV}$$

It is worth noting that the above energy release is less than that in a nuclear fission. However, its value is 26.7/4 = 6.7 MeV per nucleon as compared to less than 1 MeV per nucleon in fission process.

#### Hydrogen Bomb (Fusion Bomb).

We have already seen that the nuclear fusion reaction is a temperaturedependent reaction, *i.e.* the nuclear fusion reaction takes place only at drastically

high temperature. Such a high temperature which is necessary for bringing about nuclear fusion reaction can be obtained only by the fission of  $^{235}$ U nucleus which is an explosive chain reaction. This forms the principle of hydrogen bomb. In the preparation of hydrogen bomb a suitable quantity of all the isotopes of hydrogen  $(_{1}^{1}H, _{1}^{2}H \text{ and }_{1}^{3}H)$  is combined with an atomic bomb. The function of atomic bomb, as said above, is to provide the high temperature which is necessary for bringing about the nuclear fusion reactions in hydrogen bomb.

In hydrogen bomb the following nuclear fusion reactions take place :

$${}^{1}_{1}H + {}^{2}_{1}H \rightarrow {}^{3}_{2}He + 5 \text{ MeV}$$

$${}^{2}_{1}H + {}^{2}_{1}H \rightarrow {}^{3}_{2}He + {}^{1}_{0}n + 3.2 \text{ MeV}$$

$${}^{3}_{1}H + {}^{2}_{1}H \rightarrow {}^{4}_{2}He + {}^{1}_{0}n + 17.6 \text{ MeV}$$

$${}^{3}_{Tritium}$$

We see that in each of the above nuclear fusion reactions energy is released. Thus in hydrogen bomb isotopes of hydrogen are combined (fused) with deuterium  $\binom{2}{1}H$  and form heavier nuclei with the release of enormous energy.

Hydrogen bomb is 1000 times more powerful than the atom bomb which is based on *nuclear fission*. Its more power is due to the rapid release of a tremendous amount of energy, in the fusion reactions taking place in hydrogen bomb.

Why is H-bomb (fusion bomb) superior to atom bomb (fission bomb)?

A fusion bomb is superior to a fission bomb because of the following reasons :

(i) The energy release in a hydrogen bomb is *open-ended i.e.* it has no upper limit. It depends on how much fusible material is present in the bomb.

(*ii*) It has no limitation of a critical size of the fusible material unlike an atomic bomb. If the active material in an atomic bomb exceeds the critical size, *spontaneous* explosion results. Hydrogen bomb cannot explode unless 'ignited' *i.e.*, heated to critical ignition temperature and any amount of fusible material is safe until ignited. Thus the amount of fusible material in a hydrogen bomb is not limited.

#### **Comparison of Fission and Fusion**

(a) **Point of similarity.** One thing common between the two nuclear processes is that they release very large amount of energy.

(b) Points of dissimilarities. There are many differences in the mechanisms of the two processes.

(i) Fission involves *breaking* up of a heavy nucleus into lighter nuclei. Fusion, on the other hand, involves *combining* of two lighter nuclei into one heavy nucleus.

(*ii*) The links of the fission process are neutrons while the links of a fusion process are protons.

(*iii*) Fission proceeds best with *thermal neutrons* where thermal means room temperature. Fusion proceeds best with *thermal particles* where thermal means temperatures of millions of °K.

# Artificial Or Induced Radioactivity

## What is Artificial Radioactivity ?

There are many artificial transmutations (*i.e. nuclear reactions*) in which the product nucleus is *unstable* (*i.e. radioactive isotope*) and hence disintegrates *spontaneously* (*i.e.* by itself) like naturally occurring radioactive elements such as uranium, radium etc. to give a stable isotope of some other element. The radioactive isotope while giving the stable isotope during its disintegration, emits usually either electrons  $\binom{0}{-1}e$  or positrons  $\binom{0}{+1}e$ . The spontaneous disintegration of the radioactive isotope takes place according to the same laws that apply to the disintegration of naturally-occurring radioactive elements. Thus :

The process in which an element is converted into a new radioactive isotope (i.e. unstable isotope) by artificial means (i.e. by bombarding the element with fast moving particles like proton, deutron, helium etc) is called **artificial** or **induced radioactivity**.

#### **Discovery of Artificial Radioactivity**

*Mme. Iren Curie Joliot* (daugther of Marie Curie) and her husband, *M. Frederick Joliot* found that when  ${}^{27}_{13}$ Al was bombarded with  ${}^{4}_{2}$ He particles obtained from polonium and the energy of the ejected neutrons was measured, the detector continued to respond to some penetrating radiations, even after the polonium source was taken away. These penetrating radiations were later on found to be *positrons* ( ${}^{0}_{+1}e$ ). These observations made Curie-Joliots pair draw the conclusion that the product nucleus formed during the bombardment of  ${}^{27}_{13}$ Al by  ${}^{4}_{2}$ He particles was unstable (*i.e. radioactive*) and hence disintegrated spontaneously emitting positron and finally changing into a stable  ${}^{30}_{14}$ Si isotope.

The whole process can be shown by the following nuclear equations :

$^{27}_{13}\mathrm{Al}$ stable isotope	+ ${}^{4}_{2}\text{He} \rightarrow$	30 P unstable isotope ( <i>i.e.</i> Radioactive)	$+ \frac{1}{0}n$
$^{30}_{15}{ m P}$	$\rightarrow$	<sup>30</sup> <sub>14</sub> Si + stable isotope	$_{+1}^{0}e$ ( $t_{1/2} = 3.25$ minutes) positron

This was how the positron which is a counterpart of electron and has a unit positive charge and no mass was first discovered.

The reactions in case of  $^{24}_{12}Mg$  and  $^{10}_{5}B$  can be shown as follows :

 $(i) \begin{array}{c} {}^{24}_{12}\mathrm{Mg} + {}^{4}_{2}\mathrm{He} \rightarrow {}^{27}_{14}\mathrm{Si} + {}^{1}_{0}n \\ \mathrm{unstable\ isotope} \end{array}$   $\begin{array}{c} {}^{27}_{14}\mathrm{Si} \rightarrow {}^{27}_{13}\mathrm{Al} + {}^{0}_{+1}e \\ \mathrm{stable\ isotope} \end{array}$   $(ii) \begin{array}{c} {}^{10}_{5}\mathrm{B} + {}^{4}_{2}\mathrm{He} \rightarrow {}^{13}_{7}\mathrm{N} + {}^{1}_{0}n \\ \mathrm{unstable\ isotope} \end{array}$   $\begin{array}{c} {}^{13}_{7}\mathrm{N} \rightarrow {}^{13}_{6}\mathrm{C} + {}^{0}_{+1}e \\ \mathrm{stable\ isotope} \end{array}$ 

### **Researches on Induced Radioactivity**

As soon as Curie and Joliot announced their discovery, the study of artificial radioactivity was taken up by many other workers and new cases of it were announced at a rapid rate. It was soon found that the phenomenon occurred not only under  $\alpha$ -particle bombardment, but also with other projectiles, as protons, deuterons and neutrons and that the artificially produced radioelements not only emitted positrons but also electrons in several cases. Some examples are given below :

(i) Reactions emitting electrons  $\begin{pmatrix} 0\\-1 \end{pmatrix} e$ . Electrons are emitted in  $(n, \gamma)$ , (n, p),  $(n, \alpha)$  and (D, p) reactions.

(a) 
$$(n, \gamma)$$
  ${}^{115}_{49}\text{In} + {}^{1}_{0}n \rightarrow {}^{116}_{40}\text{In} + {}^{0}_{0}\gamma_{\text{unstable}}$   
 ${}^{116}_{49}\text{In} \rightarrow {}^{116}_{50}\text{Sn} + {}^{-0}_{-1}e \ (t_{1/2} = 13 \text{ seconds})$   
(b)  $(n, p)$   ${}^{14}_{7}\text{N} + {}^{0}_{0}n \rightarrow {}^{14}_{6}\text{C} + {}^{1}_{1}\text{H}_{\text{unstable}}$   
 ${}^{14}_{6}\text{C} \rightarrow {}^{14}_{7}\text{N} + {}^{0}_{-1}e \ (t_{1/2} = 5568 \text{ years})$   
stable  ${}^{14}_{6}\text{C} \rightarrow {}^{14}_{7}\text{N} + {}^{0}_{-1}e \ (t_{1/2} = 5568 \text{ years})$   
(c)  $(n, \alpha)$   ${}^{27}_{13}\text{Al} + {}^{0}_{0}n \rightarrow {}^{24}_{11}\text{Na} + {}^{4}_{2}\text{He}_{\text{unstable}}$   
 ${}^{24}_{11}\text{Na} \rightarrow {}^{24}_{12}\text{Mg} + {}^{0}_{-1}e \ (t_{1/2} = 15 \text{ hours})$   
stable (d)  $(D, p)$   ${}^{31}_{15}\text{P} + {}^{2}_{1}\text{H} \rightarrow {}^{32}_{15}\text{P} + {}^{1}_{1}\text{H}_{\text{unstable}}$   
 ${}^{32}_{15}\text{P} \rightarrow {}^{32}_{15}\text{S} + {}^{0}_{-1}e \ (t_{1/2} = 14.3 \text{ days})$ 

(ii) Reactions emitting positrons  $\binom{0}{+1}e$ . Positrons are emitted in  $(p, \gamma)$ , (p, n),  $(\alpha, n)$ , (D, n) and  $(\gamma, n)$  reactions.

$$\begin{array}{ll} (a) \ (p, \gamma) & \stackrel{12}{_{6}^{2}} \mathrm{C} + \frac{1}{1} \mathrm{H} \rightarrow \stackrel{13}{_{7}^{3}} \mathrm{N} + \stackrel{0}{_{0}^{3}} \gamma \\ & \stackrel{\mathrm{unstable}}{\mathrm{unstable}} \\ & \stackrel{13}{_{7}^{3}} \mathrm{N} \rightarrow \stackrel{13}{_{6}^{3}} \mathrm{C} + \stackrel{0}{_{+1}^{1}} e \ (\mathrm{T} = 10 \ \mathrm{minutes}) \\ & \stackrel{\mathrm{stable}}{\mathrm{stable}} \\ (b) \ (p, n) & \stackrel{58}{_{28}^{8}} \mathrm{Ni} + \frac{1}{_{1}^{1}} \mathrm{H} \rightarrow \stackrel{58}{_{29}^{28}} \mathrm{Cu} + \frac{1}{_{0}^{0}} n \\ & \stackrel{\mathrm{unstable}}{\mathrm{unstable}} \\ & \stackrel{58}{_{29}^{2}} \mathrm{Cu} \rightarrow \stackrel{58}{_{28}^{8}} \mathrm{Ni} + \stackrel{0}{_{+1}^{1}} e \ (\mathrm{T} = 2.6 \ \mathrm{seconds}) \\ & \stackrel{\mathrm{stable}}{\mathrm{stable}} \\ (c) \ (\alpha, n) & \stackrel{14}{_{7}^{4}} \mathrm{N} + \stackrel{4}{_{2}^{2}} \mathrm{He} \rightarrow \stackrel{17}{_{9}^{9}} \mathrm{F} + \frac{1}{_{0}^{0}} n \\ & \stackrel{\mathrm{unstable}}{\mathrm{unstable}} \\ & \stackrel{17}{_{9}} \mathrm{F} \rightarrow \stackrel{17}{_{8}^{7}} \mathrm{O} + \stackrel{0}{_{+1}^{0}} e \ (\mathrm{T} = 70 \ \mathrm{seconds}) \\ & \stackrel{\mathrm{stable}}{\mathrm{stable}} \\ (d) \ (D, n) & \stackrel{14}{_{7}^{4}} \mathrm{N} + \stackrel{2}{_{1}^{2}} \mathrm{H} \rightarrow \stackrel{15}{_{8}^{50}} + \stackrel{1}{_{0}^{0}} n \\ & \stackrel{\mathrm{unstable}}{\mathrm{unstable}} \\ & \stackrel{15}{_{8}^{6}} \mathrm{O} \rightarrow \stackrel{15}{_{7}^{7}} \mathrm{N} + \stackrel{0}{_{+1}^{0}} e \ (\mathrm{T} = 2.1 \ \mathrm{minutes}) \\ & \stackrel{\mathrm{stable}}{\mathrm{stable}} \end{array}$$

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(e) 
$$(\gamma, n)$$
  ${}^{31}_{15}P + {}^{0}_{0}\gamma \rightarrow {}^{30}_{15}P + {}^{1}_{0}n$   
unstable  
 ${}^{30}_{15}P \rightarrow {}^{30}_{14}Si + {}^{0}_{+1}e \text{ (T = 2.5 minutes)}$   
stable

# **Preparation of Transuranium Elements**

Until recently, it was believed that there are only 92 elements (Atomic number 1 to 92). As a result of study of radioactive processes, however, it was observed that atoms with atomic number higher than 92 could be produced. At present 13 elements with atomic weight higher than that of uranium (At. No. = 92) and with atomic numbers 93 to 105 are called **transuranium elements or transuranic elements** because they lie beyond uranium in the periodic table.

It was only in 1940 that the existence of these elements was definitely established.

The names, symbols and atomic numbers of these elements are given below. The numbers given on the bottom left of the symbols indicate their atomic numbers.

Neptunium ( $_{93}$ Np), Plutonium ( $_{94}$ Pu), Amercium ( $_{95}$ Am), Curium ( $_{96}$ Cm), Berkelium ( $_{97}$ Bk), Californium ( $_{98}$ Cf), Einsteinium ( $_{99}$ Es), Fermium ( $_{100}$ Fm), Mendelevium ( $_{101}$ Md), Nobelium ( $_{102}$ No), Lawrencium ( $_{103}$ Lw), Kurchatovium ( $_{104}$ Ku), and Hahnium ( $_{105}$ Ha).

<sub>93</sub>Np. In 1934 *Fermi* suggested that the bombardment of uranium with neutrons might give transuranium elements. In May 1940 *Mc Millan* and *Abelson* bombarded <sup>238</sup><sub>92</sub>U with slow neutrons and thus got a new isotope, <sup>239</sup><sub>92</sub>U which is radioactive with a half-life period of 23 minutes and hence disintegrates emitting  $\beta$ -particles (*i.e.* <sup>0</sup><sub>-1</sub>*e* or <sup>0</sup><sub>-1</sub> $\beta$ ) to produce a new element called **Neptunium**, Np with atomic number, Z = 93.

$$\begin{array}{l} {}^{238}_{92} \mathbb{U} \,+\, {}^{1}_{0} n \,\rightarrow\, {}^{239}_{92} \mathbb{U} \,\,+\, {}^{0}_{0} \gamma \,(t_{1/2} = 23.5 \,\, \mathrm{minutes}) \\ {}^{unstable}_{92} \mathbb{U} \,\rightarrow\, {}^{0}_{-1} e \,+\, {}^{239}_{93} \mathrm{Np} \,\left(Neptunium\right) \,(t_{1/2} = 23 \,\, \mathrm{minutes}) \end{array}$$

In all, 20 isotopes of neptunium have been produced with mass numbers ranging from 231 to 240 by bombarding uranium with (i) fast deuterons (up to 100 MeV energy) from a cyclotron (ii) fast neutrons and (iii) accelerated  $\alpha$ -particles.

 $_{94}$ Pu. Later on it was found that  $^{239}_{93}$ Np was also radioactive with a half-life period of 2.3 days and hence disintegrated emitting  $\beta$ -particles into another transuranium element now called **Plutonium**, Pu with Z = 94.

 $^{239}_{93}$ Np  $\rightarrow ^{0}_{-1}e + ^{239}_{94}$ Pu (*Plutonium*) ( $t_{1/2} = 2.3$  days)

The isotope of plutonium is itself an  $\alpha$ -emitter and has a half-life of 24,400 years. It is manufactured in large amounts in nuclear reactors and can be used for the production of nuclear power or atom bomb.

95Am and 96Cm. In 1945, Hamilton, Seaberg and collaborators prepared two more trans-uranium elements viz. Americium, Am with Z = 95 and Curium, Cm

with Z = 96 by the bombardment of  $^{238}_{92}U$  and  $^{239}_{94}Pu$  respectively with 40 MeV helium produced in the 60 inch Berkeley cyclotron.

 $\begin{array}{l} {}^{238}_{92}\mathrm{U} + {}^{4}_{2}\mathrm{He} \rightarrow {}^{241}_{94}\mathrm{Pu} + {}^{1}_{0}n \\ {}^{241}_{94}\mathrm{Pu} \rightarrow {}^{0}_{-1}e + {}^{241}_{95}\mathrm{Am} \; (Americium) \; (t_{1/2} = 14 \; \mathrm{years}) \\ {}^{239}_{94}\mathrm{Pu} + {}^{4}_{2}\mathrm{He} \rightarrow {}^{1}_{0}n + {}^{242}_{96}\mathrm{Cm} \; (Curium) \end{array}$ 

 $_{97}$ Bk and  $_{98}$ Cf. In 1950, *Thomson, Ghiorso* and *Seaborg* obtained **Berkelium**. Bk with Z = 97 and **Californium**, Cf with Z = 98 by bombarding  $^{241}_{95}$ Am and  $^{242}_{96}$ Cm respectively with 35 MeV helium produced in the same 60 inch cyclotron.

 $^{241}_{95}\text{Am} + {}^{4}_{2}\text{He} \rightarrow 2{}^{1}_{0}n + {}^{243}_{97}\text{Bk} (Berkelium)$ 

 $^{242}_{96}$ Cm +  $^{4}_{2}$ He  $\rightarrow 2^{1}_{0}n$  +  $^{244}_{98}$ Cf (Californium)

<sub>99</sub>Es. Ghiorso, Rossi, Harvey and Thompson under the leadership of Seaborg, bombarded  $^{239}_{92}$ U with accelerated nucleus of  $^{14}_{7}$ N to get an isotope of Einsteinium, Es with Z = 99.

 $^{239}_{92}\text{U} + {}^{14}_{7}\text{N} \rightarrow 6{}^{1}_{0}n + {}^{247}_{99}\text{Es} (Einsteinium)$ 

<sup>100</sup>**Fm.** Ghiorso, Harvey, Thompson and Choppin, under the direction of Seaborg, discovered the element, **Fermium**, Fm with Z = 100 by bombarding <sup>239</sup><sub>94</sub>Pu with neutrons from an atomic reactor.

 $^{239}_{94}$ Pu +  $15^{1}_{0}n \rightarrow 6^{-0}_{-1}e + {}^{254}_{100}$ Fm (*Fermium*)

 $^{250}_{100}$  Fm isotope can be prepared by bombarding  $^{238}_{92}$  U with accelerated nucleus of  $^{16}_{8}$  O.

 $^{238}_{92}\text{U} + {}^{16}_{8}\text{O} \rightarrow 4{}^{1}_{0}n + {}^{250}_{100}\text{Fm} (Fermium)$ 

 $_{101}$ Md. In April 1955, *Seaborg*, *Ghiorso* and coworkers discovered Mendelevium, Md with Z = 101 by bombarding  $_{99}^{253}$ Es with 48 MeV helium ions.

 $^{253}_{99}$ Es +  $^{4}_{2}$ He  $\rightarrow ^{1}_{0}n$  +  $^{256}_{101}$ Md (Mendelevium)

<sup>102</sup>No. This element is an  $\alpha$ -emitter. Very recently (in 1957) the Noble Institute of Physics Stockholm obtained the element Nobelium, No with Z = 102 by bombarding <sup>246</sup><sub>96</sub>Cm with accelerated <sup>12</sup><sub>6</sub>C ions. Russian scientists have proposed the name Joliocium for nobelium.

 $^{246}_{96}$ Cm +  $^{12}_{6}$ C  $\rightarrow 6^{1}_{0}n$  +  $^{252}_{102}$ No (Nobelium)

This element is an  $\alpha$ -emitter and has a half-life period on 10 to 12 minutes. <sup>103</sup>Lw. The element, Lawrencium, Lw with Z = 103 has been prepared by bombarding <sup>251</sup><sub>98</sub>Cf with accelerated <sup>10</sup><sub>5</sub>B ions.

 $^{251}_{98}\text{Cf} + {}^{10}_{5}\text{B} \rightarrow 4{}^{1}_{0}n + {}^{257}_{103}\text{Lw} (Lawrencium)$ 

 $_{104}$ Ku and  $_{105}$ Ha. Kurchatovium. Ku with Z = 104 and Hahnium, Ha with Z = 105 are the latest addition to the list of transuranium elements. American scientists have suggested the name *Rutherfordium* for the element with Z = 104.

#### **Uses of Radioisotopes**

Some important uses of radioisotopes are given below :

# 1. Uses of Radioisotopes as Radioactive Tracers.

First of all we should understand: "What are radioactive tracers ?" Radioactive isotopes have a property due to which they can easily be detected and estimated quantitatively. Further, they reach almost exactly as the corresponding nonradioactive isotopes do. As such, if we want to trace the course of an atomic species in a chemical or a physical change, we mix a small quantity of the radioactive isotope with non-radioactive isotope. Here we say that the radioactive istope is acting as a **Radioactive tracer** or **Radioactive indicator** or simply as **Labelled** or **Tagged element.** The presence of radioactive tracer is later on detected in the products with the help of sensitive instruments. Some important uses of radioactive tracers are given below :

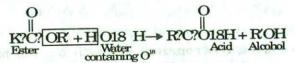
(i) Uses of tracers in studying reaction mechanisms. (a) Photosynthesis. The mechanism of the process of photosynthesis taking place in plants has been studied by reacting carbon dioxide containing <sup>18</sup>O ( $CO_2^{18}$ ) with H<sub>2</sub>O. In this process the green plants take up CO<sub>2</sub> and H<sub>2</sub>O in presence of sunlight and chlorophyll to form sugar and starch, giving out oxygen gas.

 $6\mathrm{CO}_2 + 6\mathrm{H}_2\mathrm{O} \rightarrow \mathrm{C}_6\mathrm{H}_{12}\mathrm{O}_6 + 6\mathrm{O}_2$ 

Here a very important question arises—whether the oxygen evolved in this process comes from  $CO_2$  or from  $H_2O$  or from both. This question has been answered by the use of radioactive <sup>18</sup>O isotope. What we do is that  $H_2O$  is made to react with carbon dioxide containing <sup>18</sup>O (*i.e.*  $CO_2^{18}$ ) and it is found that the oxygen evolved does not contain <sup>18</sup>O, *i.e.*, O<sup>18</sup> present in  $CO_2^{18}$  goes to sugar and water while that of water is evolved as free oxygen. Thus oxygen evolved in the process of photosynthesis comes from  $H_2O$  and not from carbon dioxide and consequently, the reaction shown above should be shown as :

 $6{\rm CO_2}^{18} \, + \, 12{\rm H_2O} \rightarrow {\rm C_6H_{12}O^{18}} + \, 6{\rm H_2O^{18}} + \, 6{\rm O_2}$ 

(b) Hydrolysis of ester. Mechanism of ester hydrolysis has been studied by using  $O^{18}$  isotope. It is observed that when an ester is hydrolysed by water containing  $O^{18}$  (*i.e.*  $H_2O^{18}$ ), the alcohol formed does not have any  $O^{18}$  while the acid has the whole of it. The presence of  $O^{18}$  in the acid proves that the—OR' group in the ester is wholly replaced by — $O^{18}H$  group in  $H_2O^{18}$ . Thus the hydrolysis should correctly be shown as :



(*ii*) **Use of tracers in the diagnosis of diseases.** Radioisotopes have proved very useful in the diagnosis and understanding many of the diseases. Some examples are given below :

(a) Location and detection of brain tumour. Labelled iodine has been used to locate and detect the presence of tumour. To locate it a small quantity of

radioisotope of iodine mixed with an organic dye is injected into the body of the patient. Dye with radioisotope is strongly absorbed by the tumour and radiations are produced. Detection of these radiations gives valuable information regarding the limits of the growth and location of the tumour.

(b) Circulation of blood. Radiosodium,  $Na^{24}$  ( $t_{1/2} = 15$  hours,  $\beta$ -particle emitter) has been used to study cases of restricted circulation of blood. A small quantity of NaCl solution which contains labelled-sodium ( $Na^{24}$ ) is injected into, the vein of a patient's forearm and a  $\gamma$ -ray detector is then placed in contact with one of his feet. If blood circulation is normal, the presence of rodioactivity is soon discovered in the foot. It increases rapidly and becomes maximum within an hour. However, if there is any circulatory impairment, radioactivity will increase slowly showing that blood has some difficulty in reaching the foot. By moving the detector to different parts of the body, the position of restriction can be located and the necessary treatment applied.

(c) Pumping action of heart. Pumping action of heart has been studied by using radiosodium or radioiodine. A small quantity of labelled NaCl solution is injected into the blood stream and a detector, attached to an automatic pen recorder, is placed on the heart. As radiosodium enters the right side of the heart (i.e. atrium), the pen of the recorder rises and then drops as the venous blood enters the lungs for oxygenation. After some time, the radiosodium appears with the arterial blood on left side of the heart (*i.e.* ventricle) and there is another rise and fall of the recording pen. By examining the resulting curve, the pumping action of the two sides of the heart can be compared and abnormalities, if any, can be discovered.

(d) Functioning of thyroid gland. Radioisotope of iodine,  $I^{131}$  with  $t_{1/2} = 8$  days is given to a patient with thyroid disorders. It decays  $\beta$ -rays. Detection of these rays gives an information regarding the functioning of the thyroid gland.

(e) Disorders associated with pregnancy. Tracer iron has been used in studying the disorders associated with pregnancy.

(f) Test of cancer growth.  ${}^{50}$ Co emits high energy  $\gamma$ -rays which are used for testing deeply seated cancer growth.

(*iii*) Uses of tracers in industry. Radioactive isotopes have found many applications in industry both in research and in process control. Some of the examples are given below :

(a) Determination of the wear of piston rings. The wear of piston rings and of gears in engines and its prevention by means of suitable lubricants have been studied by radioactivity. A steel piston ring is made radioactive by exposing it to neutrons in a nuclear reactor. The piston ring is then fitted into the cylinder of an internal combustion engine which is operated normally with a particular lubricating oil. By determining the rodioactivity removed by the oil, the amount of piston wear can be determined.

(b) Self-diffusion of metals. The phenomenon of self-diffusion in metals *i.e.* the movement of the atoms of a metal within the crystal lattice has been studied with the help of isotopes.

(c) Uniform mixing. Uniformity of mixing during the blending of petrols, lubricating oils and greases etc. has been achieved by labelling one of the constituents with a radioactive tracer.

(d) As catalyst.  $\gamma$ -rays obtained from  $Co^{60}$  have been used as catalyst in the manufacture of  $C_2H_5$  Br from ethylene and HBr.

(e) **Treatment of a metal.** By incorporating radioactive isotope in the metal it is possible to know as to what happens when a metal is subjected to a particular treatment like age-hardening, annealing, quenching, coldroling etc.

(f) Mechanism of lubricants. Radioactive isotopes have been used in studying the mechanism of the effectiveness of various lubricants.

(g) Mechanisms of reactions. Radioactive carbon,  $C^{15}$  has been used as a tracer in studying mechanisms involved in many reactions of industrial importance such as alkylation, polymerisation, catalytic synthesis, etc.

(*iv*) Uses of tracers in agriculture. (a) Uptake of phosphorus by plants. When a plant grows, it absorbs phosphorus both from the soil and from the added phosphatic fertilizer. In order to check the usefulness of the fertilizer, it is important to know what proportion of phosphorus comes from each source. Ordinary analytical methods cannot answer this question because phosphorus from both sources is exactly the same. However, if radiophosphorus ( $P^{32}$ ) is added in the phosphatic fertilizer, the exact proportion taken up by the plant can be determined accurately.

The efficiency of different phosphatic fertilizers can be compared with the help of radioactive phosphorus being used as a tracer element. Fertilizer which is absorbed quickly is more efficient.

(b) Transportation of mineral in plants. The transportation of mineral from roots to leaves and its subsequent redistribution within the plants can be followed through the use of radioactive isotopes by means of radioautography. By this technique the distribution of  $S^{35}$ , supplied in the form of sulphate, in sugar beet plants has been followed.

(c) Irradiation of maize with radioactive cobalt produces 15% increase in the quantity of green part over those plants growing in the same field, but not irradiated. In some cases, solutions of radioactive substances are used in place of irradiation. The seeds are dipped in these solutions before planting. This also raises the yield of cane sugar, wheat, maize etc.

(v) Uses of tracers in analytical chemistry. Suppose we want to determine the solubility of  $PbSO_4$  in water. A known quantity of *radioactive* lead (Pb<sup>\*</sup>) is mixed with ordinary lead (Pb) in a known proportion. The entire amount consisting of radioactive and ordinary lead is dissolved in dil. HNO<sub>3</sub> and then precipitated as lead sulphate on the addition of dil. H<sub>2</sub>SO<sub>4</sub>.

 $\mathbf{Pb^{*} + Pb} \xrightarrow{\mathbf{HNO}_{3}} \mathbf{Pb^{*}(NO_{3})_{2} + Pb(NO_{3})_{2}} \xrightarrow{\mathbf{H}_{2}\mathbf{SO}_{4}} \mathbf{Pb^{*}SO_{4}} \downarrow + \mathbf{PbSO}_{4} \downarrow$ 

After filtration, the radioactivity of the solution is measured and thus the amount of lead sulphate present in solution is calculated. This, of course, gives the amount of radioactive lead present in solution. If the ratio of the two varieties

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of lead originally taken is known, the amount of ordinary lead present in solution can be calculated.

# 2. Uses of Radioisotopes in the Treatment of Diseases (Radiotherapy).

The treatment of diseases by the use of radioisotopes is called *Radiotherapy*. Some examples of radiotherapy are given below :

(a) Treatment of thyroid complaints. Radioactive iodine  $I^{131}$  has been used for the treatment of certain thyroid complaints. Stable iodine and radioactive iodine are preferentially absorbed by the thyroid gland. This fact is utilised in the treatment of hyperthyroidism and cancer of the thyroid. Radioactive iodine destroys abnormal tissues in the thyroid gland more rapidly and in this way checks the abnormal growth.

(b) Treatment of blood disorders. Radioactive phosphorus in the from of phosphate is widely used in the treatment of certain blood disorders.

(c) Treatment of cancer growth. Radiocobalt (Co<sup>60</sup>) produced by the action of neutrons from a nuclear pile,  $t_{1/2} = 5.3$  days,  $\gamma$ -rays emitter and radiogold (Au<sup>198</sup>), T = 3 days,  $\gamma$ -rays emitter are used in the treatment of some forms of cancer. Co<sup>60</sup> has been called *Poor Man's Radium*.

(d) Treatment of leukemia. Radioisotope of phosphorus is being used for the treatment of leukemia.

(e) Treatment of skin diseases. Radiophosphorus (P<sup>30</sup>),  $t_{1/2} = 14.3$  days,  $\beta$ -emitter is found good for skin diseases.

3. Determination of the Age of the Earth by Rock Dating Method The age of a rock (*i.e.* the time that elapsed since the rock crystallied from the molten state) gives an approximate idea of the age of the earth provided that it is assumed that the rock or the mineral under examination is as old as the earth. Let us consider a rock containing U-238 isotope formed many years ago. The age of this rock can be determined by considering its radioactive disintegration which, as we have already seen, is governed by the relation

$$N = N_0 e^{-\lambda t}, \qquad (i)$$

where  $N_0$  = amount of U-238 isotope originally present in a small quantity of the rock or mineral at the time the rock was formed, N = Amount of U-238 still left undecayed after the lapse of time, t which represents the age of the rock, and  $\lambda$  = disintegration constant of U-238.

U-238 started to decay giving rise to U-238—Pb-206 series. Some of its quantity decayed into Pb-206 in time, t, while the remaining quantity of U-238 remained undisintegrated. If the quantity of U-238 remained undisintegrated is  $U^{238}$  (*i.e.*  $U^{238}$  represents the quantity of U-238 existing at the present time in the rock) and that of Pb-206 formed as a result of disintegration of U-238 is Pb<sup>206</sup> (*i.e.* Pb<sup>206</sup> represents the quantity of Pb-206 existing at present in the rock), then the quantity of U-238 present at zero time (*i.e.* before disintegration started) is equal to (U<sup>238</sup> + Pb<sup>206</sup>). Thus :

$$N = U^{238}$$
 and  $N_0 = (U^{238} + Pb^{206})$ 

and hence eqn. (i) given above becomes :

$$U^{238} = (U^{238} + Pb^{206}) e^{-\lambda t}$$

 $=\left(1+\frac{Pb^{206}}{U^{238}}\right)$ 

$$TT^{238} = (TT^{238} + TT^{238})$$

11238

or

$$\frac{1}{e^{\lambda t} + Pb^{206}} = e^{-\lambda t}$$
$$e^{\lambda t} = \frac{U^{238} + Pb^{206}}{U^{238}}$$

or

Now we know that the value of decay constant  $(\lambda)$  of U-238 is given by :

 $\lambda t = 2.303 \ \log_{10} \left( 1 + \frac{\mathrm{Pb}^{206}}{\mathrm{U}^{238}} \right)$ 

$$\lambda = \frac{0.693}{t_{1/2}}$$

where  $t_{1/2}$  is the half-life period of U-238.

Thus

$$t = \frac{2.303 \ t_{1/2}}{0.693} \log_{10} \left( 1 + \frac{\text{Pb}^{206}}{\text{U}^{238}} \right)$$

Since the values of Pb<sup>206</sup> and U<sup>238</sup> can be determined experimentally, the value of t which is the age of the rock (or of earth) can be found out.

If, in place of rock containing U-238, we consider the rock containing U-235, then the isotope of lead obtained from the disintegration of U-235 is Pb-207 and the relation (ii) reduces to (iii) given below :

$$U^{235} = (U^{235} + Pb^{207}) e^{-\lambda' t} \qquad \dots (iii)$$

where  $\lambda'$  is the disintegration constant of U-235 isotope.

Now equation (ii) can also be written as :

$$\frac{\mathbf{U}^{238}}{\mathbf{U}^{238}} = \left(\frac{\mathbf{U}^{238}}{\mathbf{U}^{238}} + \frac{\mathbf{Pb}^{206}}{\mathbf{U}^{238}}\right) e^{-\lambda t}$$

$$\mathbf{1} = \left(\mathbf{1} + \frac{\mathbf{Pb}^{206}}{\mathbf{U}^{238}}\right) e^{-\lambda t}$$

$$e^{\lambda t} = \mathbf{1} + \frac{\mathbf{Pb}^{206}}{\mathbf{U}^{238}}$$

$$(e^{\lambda t} - \mathbf{1}) \mathbf{U}^{238} = \mathbf{Pb}^{206}$$

or

or

or

I

$$(e^{\lambda' t} - 1) U^{235} = Pb^{207}$$

On dividing equations (iv) and (v) by each other, we get

$$\frac{\mathrm{Pb}^{206}}{\mathrm{Pb}^{207}} = \frac{\mathrm{U}^{238}(e^{\lambda t} - 1)}{\mathrm{U}^{235}(e^{\lambda' t} - 1)}$$

The present ratio, U238/U235 is known to be 139 and hence

...(ii)

$$\frac{\mathrm{Pb}^{206}}{\mathrm{Pb}^{207}} = \frac{139 \left(e^{\lambda t} - 1\right)}{\left(e^{\lambda t} - 1\right)}$$

When the values of  $\lambda$  and  $\lambda'$  as determined from the half-life periods of the isotopes viz. U-238 and U-235 and the ratio Pb<sup>206</sup>/Pb<sup>207</sup> as determined by a mass spectrometer are put in the above equation, we get the value of t which is the age of the rock or earth.

The above method is useful for dating minerals and rocks of considerable age.

**Example.** The ratio of mass of  $Pb^{206}$  to the mass of  $U^{238}$  in a certain rock specimen is found to be 0.5. Assuming that the rock originally contained no lead, estimate its age. Half-life of uranium is  $4.5 \times 10^9$  years.

Solution. We have already seen that the relation between the existing masses of U<sup>238</sup> and Pb<sup>206</sup> in any rock specimen is given by :

$$U^{238} = (U^{238} + Pb^{206})e^{-\lambda t}$$

$$1 = \left(1 + \frac{Pb^{206}}{U^{238}}\right)e^{-\lambda t}$$

$$1 = (1 + 0.5)e^{-\lambda t} = 1.5e^{-\lambda t}$$

$$e^{\lambda t} = 1.5$$

$$\lambda t = 2.3 \log_{10} 1.5 = 2.3 \times 0.1761$$

$$\frac{0.693}{.5 \times 10^9} \times t = 0.23 \times 0.1761$$

or

or

or

...

 $t = 2.63 \times 10^9$  years

4. Determination of the Age of Recent Objects by Radiocarbon **Dating Method.** 

The age of recent objects such as those of animal or vegetable origin like a piece of wood or animal fossil can be determined by radio-carbon dating method, since rock dating method is useful only for the minerals or rocks of considerable age. This method was developed by Willard Libby who was awarded Nobel Prize for this brilliant work.

The determination of the age of a sample of wood (i.e. the time which elapsed after the death of the living plant) consists of determining the ratio of the amount of  ${}_{6}C^{14}$  to that of  ${}_{6}C^{12}$  in both the pieces of wood, i.e. in fresh (living) piece and dead (cut) piece. We know that the atmospheric carbon dioxide is a mixture of  $C^{14}O_2$  and  $C^{12}O_2$  which are present in a fixed ratio. Plants absorb carbon dioxide from the atmosphere and prepare cellulose (wood). As long as the plant is alive, the ratio of  ${}_{6}C^{14}$  to  ${}_{6}C^{12}$  atoms in the wood of the plant is the same as in the atmosphere but when the tree is cut (*i.e.* when the plant dies), the ratio of  ${}_{6}C^{14}$ to  ${}_{6}C^{12}$  begins to decrease continuously due to the continuous decrease in the amount of  ${}_{6}C^{14}$  in the plant. This decrease in the amount of  ${}_{6}C^{14}$  is due to its continuous disintegration emitting β-radiations as shown :

 $_{6}C^{14} \rightarrow _{7}N^{14} + \beta$ -particle ( $t_{1/2} = 5568$  years) Now we know that :

$$\begin{split} N &= N_0.e^{-\lambda t} \\ t &= \frac{2.303 \text{ T}}{0.693} \log_{10} \frac{N_0}{N} \end{split}$$

or

On putting  $N_0 = C^{14}/C^{12}$  ratio in the living (*i.e.* fresh) plant,

and  $N = C^{14}/C^{12}$  ratio in the dead (*i.e.* cut) plant, in the above equation, the age of the wood, t is given by :

$$t = \frac{2.203 \ t_{1/2}}{0.693} \log \left[ \frac{C^{14}/C^{12} \ \text{ratio in the living fresh plant}}{C^{14}/C^{12} \ \text{ratio in the dead plant}} \right] \qquad \dots(i)$$

Here  $t_{1/2}$  is half-life period of  ${}_{6}C^{14}$ 

If the ratio of the amounts of  $C^{14}$  isotope in the fresh and dead wood is known, then

$$t = \frac{2.303 \ t_{1/2}}{0.693} \log \left[ \frac{\text{Amount of } C^{14} \text{ in living (fresh) wood}}{\text{Amount of } C^{14} \text{ in dead wood}} \right] \qquad \dots (ii)$$

**Example 1.** The amount of  ${}_5C^{14}$  isotope in a piece of wood is found to be onesixth present in a fresh piece of wood. Calculate the age of wood. Half-life of  ${}_6C^{14}$ = 5577 years.

Solution. With the help of equation (ii) given above we get

$$t = \frac{2.303 \times 5577}{0.693} \log \frac{1}{1/6}$$
$$= \frac{2.303 \times 5577}{0.693} \log 6$$
$$= \frac{2.303 \times 5577 \times 0.7782}{0.693}$$
$$t = 20170 \text{ years}$$

**Example 2.** A piece of wood was found to have  $C^{14}/C^{12}$  ratio 0.7 times that in a living plant. Calculate the period when the plant died. Half-life of  $C^{14} = 5760$  years.

Solution.  $t = \frac{2.303 \text{ T}}{0.693} \log \frac{1.00}{0.70}$  $= \frac{2.303 \times 5760 \times 0.155}{0.693}$  $\therefore$  t = 2970 years

**Example 3.** The  $C^{14}$  to  $C^{12}$  ratio in a certain piece of wood is 13% that of the atmosphere. Calculate the age of wood. given that half-life of  $C^{14} = 5580$  years.

Solution. We know that

$$t = \frac{2.303 \times t_{1/2}}{0.693} \log \frac{100}{13}$$

Therefore, in this case

$$t = \frac{2.303 \times 5580 \times 0.8161}{0.693}$$
$$t = 16430 \text{ years}$$

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#### **Questions with Answers**

Q.1 If the energy released in the reaction,  $4_1^1 H \rightarrow {}_2^4 He + 2_1^0 e$  is  $26 \times 10^8$ KJ mol<sup>-1</sup> of He, calculate the magnitude of the change in mass (m) in g mol<sup>-1</sup> of He.

Ans : Energy released of He

 $= 26 \times 10^8 \text{ kJ mol}^{-1}$  $= 26 \times 10^8 \times 10^3 \text{ J mol}^{-1}$  $= 26 \times 10^{11} \text{ J mol}^{-1}$ 

Now we know that change in mass (m) is given by :

$$\mathbf{E} = mc^2$$

$$m = \frac{\mathbf{E}}{c^2}$$

$$m = \frac{\mathbf{E}}{c^2}$$

$$m = \frac{\mathbf{E}}{c^2}$$

or

Now put  $E = 26 \times 10^{11} \text{ J mol}^{-1}$  and  $c = 3 \times 10^8 \text{ ms}^{-1}$  in equation (i) to get :

$$m = \frac{26 \times 10^{11} \text{ J mol}^{-1}}{(3 \times 10^8)^2 m^2 s^{-2}}$$
  
= 2.9 × 10<sup>-5</sup>  $\frac{\text{J}}{m^2 s^{-2}}$  mol<sup>-1</sup>  
= 2.9 × 10<sup>-5</sup> kg mol<sup>-1</sup> (: 1J = kg m  
= 2.9 × 10<sup>-5</sup> × 10<sup>3</sup> g mol<sup>-1</sup>  
= 0.029 g mol<sup>-1</sup>

 $(:: 1J = kg m^2 s^{-2})$ 

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Now since energy is released in the given reaction, mass of products < mass of reactants. Hence the value of m should be negative, *i.e.* change in mass (m) = $-0.029 \text{ g mol}^{-1}$  (Ans)

Q.2 Find out the value of binding energy per nucleon of  ${}_{2}O^{16}$ , if the binding energy of 8016 is 127 Mev.

Ans: The symbol,  ${}_{8}O^{16}$  shows that the number of nucleons in  ${}_{8}O^{16} = 16$  Thus: Binding energy of <sub>8</sub>O<sup>16</sup> per nucleon

$$= \frac{\text{Binding energy of }_8\text{O}^{16}}{\text{No. of nucleons in }_8\text{O}^{16}}$$
$$= \frac{\text{Binding energy of }_8\text{O}^{16}}{\text{Mass number of }_8\text{O}^{16}}$$
$$= \frac{127}{16} \text{MeV} = 7.94 \text{ MeV (Ans.)}$$

Q.3 Find out the age of artifact, if the artifact and a freshly cut down tree give 7.6 and 15.2 counts min<sup>-1</sup> g<sup>-1</sup> of carbon ( $t_{1/2} = 5760$  yrs).

Ans: The age of the artifact (t) is given by :

 $t = \frac{2.303}{\lambda} \log \frac{\text{No. of counts of freshly cut tree}}{\text{No. of counts of artifact}}$ 

...(i)

 $\lambda$  is given by :

$$t = \frac{0.693}{t_{1/2} \text{ of carbon}} = \frac{0.693}{5760 \text{ yrs}} = \frac{0.693}{5760} \text{ yrs}^{-1}$$

Put the value of  $\lambda$  in equation (i)

$$t = \frac{2.303}{0.693/5760 \text{ yrs}^{-1}} \log \frac{15.2}{7.6}$$
$$= \frac{2.303 \times 5760}{0.693} \log 2 \text{ yrs}$$
$$= 5761 \text{ yrs (Ans.)}$$

Q.4 Find out the value of binding energy of  ${}_{4}^{9}X$  per nucleon, if its mass defect is 0.090 amu. (1 amu = 931.5 Mev).

Ans : Binding energy of  ${}^{9}_{4}X$  per nucleon

$$= \frac{\text{Mass defect in amu } \times 931.5 \text{ MeV}}{\text{No. of nucleons in } {}_{4}^{9}\text{X}}$$
$$= \frac{0.090 \times 931.5}{9} \text{ MeV} = 9.315 \text{ MeV. (Ans.)}$$

Q.5 Mass of  ${}_{3}^{7}$ Li is 7.016005 amu. Mass of a proton = 1.007277 amu and mass of a neutron = 1.008665 amu. Find out the mass defect of  ${}_{3}^{7}$ Li nucleus.

**Ans**: No. of protons in  ${}^{7}_{3}\text{Li} = 3$ No. of neutrons in  ${}^{7}_{3}\text{Li} = 7 - 3 = 4$ 

 $\therefore$  Mass defect of <sup>7</sup><sub>3</sub>Li nucleus

= (Mass of 3 protons + Mass of 4 neutrons) - Mass of <sup>7</sup><sub>3</sub>Li nucleus

 $= (3 \times 1.007277 + 4 \times 1.008665) - 7.016005$ 

= 3.021831 + 4.034660 - 7.016005

= 7. 056491 - 7.016005 = 0.040486 amu (Ans.)

Q.6 Calculate the magnitude of energy released per atom of He in the nuclear fusion :  ${}_{1}^{2}H + {}_{1}^{2}H \rightarrow {}_{2}^{4}He$  (given that mass of  ${}_{1}^{2}H = 2.014$  amu and mass of  ${}_{2}^{4}He = 4.003$  amu).

Ans :	$^{2}_{1}H$	+	$^{2}_{1}H$	$\rightarrow$	$\frac{4}{2}$ He
	2.014 amu		2.014 amu		4.003 amu
	=	4.02	8 amu		4.003 amu
∴ Mas			of reactants – 4.003) an		Mass of products
	= 0.0				
: Ene	ergy release	d pe	er atom of H		= [Mass lost (in amu) × 931] Mev = 0.025 × 931 Mev

= 23.275 Mev (Ans.)

Q.7 Calculate binding energy of  $^{16}O$  (in J mol<sup>-1</sup>), if its mass defect is 0.210 amu.

Ans : Binding energy = Mass defect × 931 MeV

= 
$$0.210 \times 931$$
 MeV  
= 195.5 MeV  
=  $195.5 \times 10^{6} \times eV$   
=  $195.5 \times 10^{6} \times 1.602 \times 10^{-19} \times 6.02 \times 10^{23}$  Jmol<sup>-1</sup>  
=  $1.89 \times 10^{13}$  Jmol<sup>-1</sup>

Q.8 If the number of atoms of parent element and daughter element after time t in a transformation process is P and D respectively, then t is given by :

$$t=\frac{1}{\lambda}\ln\left(1+\frac{\mathbf{D}}{\mathbf{P}}\right)$$

#### Prove this relation ( $\lambda$ = Diseintegration constant).

**Ans**: Suppose the number of atoms of parent element in the beginning (*i.e* at t = 0) is N<sub>0</sub> and after time t the number of atoms of parent element is N. Thus the number of atoms of daughter element at time t = 0 is zero and after time t the number of atoms of daughter element is N<sub>0</sub> - N. Hence :

Parent element  $\rightarrow$  Daughter element

...(ii)

No. of atoms at $t = 0$	No	zero	and the fit where
No. of atoms after time, $t$	N = P	$(\mathbf{N}_0 - \mathbf{N}) = \mathbf{D}$	The search and
Above transformation process	shows that :		
P - N		(1)	and the state of the

(	01	r	
2	-		

or

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and

Now we know that t, in terms of N<sub>0</sub> and N, is given by :

$$t = \frac{1}{\lambda} \ln \frac{N_0}{N} \qquad \dots (iii)$$

Put N = P and N<sub>0</sub> = D + P from equations (i) and (ii) respectively in equation (iii) to get :

$$t = \frac{1}{\lambda} \ln \frac{D+P}{P}$$
$$= \frac{1}{\lambda} \ln \left(1 + \frac{D}{P}\right)$$

 $D = N_0 - N$ 

 $D = N_0 - P$  $N_0 = D + P$ 

Q.9 What is the binding energy of  ${}^{11}_5$ B nucleus if its mass defect is 0.08181 amu.

**Ans** : Binding energy of  ${}^{11}_{5}B$  nucleus = (Mass defect in amu × 931.5) Mev

= 0.08181 × 931.5 MeV = 76.20 MeV (Ans) Q.10 Find out the packing fraction of  $^{238}_{92}$ U, if its isotopic mass is 238.125 amu.

Ans : Packing fraction of  $^{238}_{92}$ U

$$= \frac{\text{Isotopic mass of } {}^{238}_{92}\text{U} - \text{Mass number of } {}^{238}_{92}\text{U}}{\text{Mass number of } {}^{238}_{92}\text{U}} \times 10^4$$
$$= \frac{238.125 - 238}{238} \times 10^4 = 5.25 \text{ (Ans.)}$$

# University Questions

- Calculate the mass defect and binding energy in MeV of oxygen isotope, <sup>16</sup>/<sub>8</sub>0 whose mass number is 15.99491 amu. Given that mass of electron = 0.0005486 amu, mass of a proton = 1.007277 amu, mass of a neutron = 1.008665 amu. (Delhi 99)
- 2. Write a note on "Nuclear fusion". (Kanpur 99)
- 3. Name the elements which are used as nuclear fuels. Explain their action. (*Himachal Pradesh 99*)
- 4. (a) What is role of meson in the nucleus of an atom?(b) Write a note on "Packing Fraction". (Allahabad 99)
- 5. Write short notes on (i) Transuranic elements (ii) Uranium as nuclear fuel. (Himachal Pradesh 2000)
- 6. What are nuclear reactions ? Describe nuclear reactions with deutrons, neutrons, tritones and photons with suitable examples. (Kumaon 2000)
- 7. Discuss the stability of nucleus on the basis of : (i) n/p ratio (ii) odd-even rule. (Lucknow 2000)
- 8. (a) Explain "Nuclear Reactor".
  - (b) Derive an expression for the disintegration constant of a radioactive element and show that decay of the element is exponential.
  - (c) The amount of  $C^{14}$  in a sample of wood is found to be one-fourth of its amount present in a fresh piece of wood. Calculate the age of the wood. (Half life = 5580 yrs.)
  - (d) How much energy in MeV is released in the formation of He nucleus (mass = 4.0017 amu)? Given  $m_n = 1.0087$ , amu  $m_p = 1.0072$  amu
  - (e) Write a note on carbon dating. (Lucknow 2001)
- 9. Describe fundamental particles of nucleons. or what are nucleons? (Kurushetra 2002)
- 10. Describe the Meson theory of stability of nucleus. (Kurushetra 2002)
- 11. Describe different methods of detection and measurement of radioactivity. (*Guwahati 2002*)
- 12. What are diffirent types of nuclear reactions depending on transformation of nucleus. (Guwahati 2002)

Nuclear Transmutations and Artificial Radioactivity

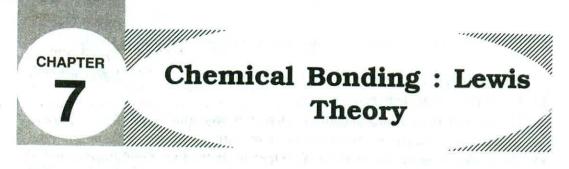
13. Discuss theory of radioactive disintegration with suitable examples.

- 14. Define artificial radioactivily with on example.
- 15. (a) What are nuclear reactions ?
  - (b) Explain Bohr's mechanism of nuclear reactions.
  - (c) Classify nuclear reactions based on energy.
- 16. What do you mean by artificial transformation and artificial radioactivity ? Give two reactions of each type. (Meerut 2008)
- 17. (a) Discuss nuclear reactions in detail.
  - (b) Define nuclear fission.

(Meerut 2009)

(Culcutta 2005)

(Meerut 2006)



## What is Chemical Bond?

Atoms rarely occur in the free state at ordinary temperature. Except noble gases, which are chemically unreactive, atoms of all other elements have a tendency to combine either with each other or with the atoms of other elements to form cluster or aggregates of atoms with definite composition. A cluster formed may be either a molecule or an ion. The attraction between atoms forming the cluster is called a *chemical bond* or *valence bond*. Thus :

A chemical bond is defined as the attractive force that holds two or more atoms together in a molecule or an ion.  $\mathbf{H}$ 

Our main concern in this chapter is to consider the interactions between atoms in the light of the structure of atom and find out the answers of the following questions

(a) Why do atoms combine?

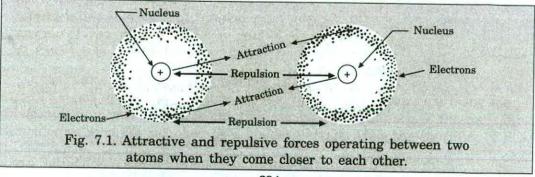
(b) How do atoms combine together?

(c) How can the properties of compounds be understood and determined in terms of the forces that keep the atoms together in molecules.

## Why Do Atoms Combine? (Cause of Chemical Bonding)

By a close study of atoms and molecules it has been found that atoms combine chemically for the following reasons :

1. Net attractive force between atoms. Atoms consist of strongly positive nucleus and negative electrons. When two atoms come closer to combine with each other to form a bond between them, the attractive and repulsive forces begin to operate between them. The attractive forces are between the electrons of one atom and the nucleus of the other atom while the repulsive forces are between the electrons or the nuclei of the two atoms (Fig. 7.1).



When the two atoms approach closer to each other, these forces counteract each other. The net result of these forces may be either attraction or repulsion between the atoms. If the attractive forces become dominant over the repulsive forces, the net result is the attraction between the atoms and hence they combine together to form a chemical bond between them. On the other hand if the repulsive forces become dominant over the attractive forces, the atoms do not combine and hence no chemical bond is established between them. For example in case of hydrogen atoms, the net result is attraction and hence two H-atoms combine together to form  $H_2$  molecule. On the other hand in case of helium atoms, the net result is repulsion and hence two He-atoms do not combine together to form  $He_2$  molecule.

2. Octet rule or rule of eight. (Electronic Theory of valency or octet theory of valency). Lewis, Kossel and Longmuir (1916) tried, for the first time, to explain why atoms combine together on the basis of the electronic configuration of noble gases as given below.

Noble gas	At. No.	Electronic configuration
He	2	ne 2 sidt og a fanne i
Ne	10	2, 8
Ar	18	2, 8, 8
Kr	36	2, 8, 18, 8
Xe	54	2, 8, 18, 18, 8
Rn	86	2, 8, 18, 32, 18, 8

They assumed that since the atoms of noble gases do not normally react with other atoms to form compounds, it is reasonable to assume that the outermost shell configuration of the atoms of noble gases is a stable configuration of 8 electrons which they called an octet. They also concluded that the two electrons in case of helium (called duplet) is also as stable as an octet present in other noble gases. Since the octet of electrons is so stable in the gases, one can reasonably assume that when atoms of other elements combine to form a molecule, the electrons in their outermost orbits are arranged between themselves in such a way that they achieve an octet of electrons which is stable and thus a chemical bond is established between the atoms.

The tendency of the atoms to have eight electrons in their outermost shell is known as octet rule or rule of eight. Since helium atom has only two electrons, this rule is called **doublet rule** or **rule of two** in case of helium. Octet rule was given in the form of a theory which is known as octet theory of valency or electronic theory of valency which states that :

In the formation of a chemical bond atoms interact with each other by losing, gaining or sharing of electrons so as to acquire a stable outer-shell of eight electrons.

The main points of this theory can be summarised as follows :

(i) Atom with 8 electrons in the outer most shell (2 in case of helium) are chemically stable and hence are incapable of chemical combination.

(ii) An atom having less than 8 electrons it its outer-most shell is chemically active and hence has a tendency to combine with other atoms. The atoms possessing less than 4 electrons in their ultimate shell usually tend to lose them, while those having more the 4 electrons in the outermost shell tend to gain the electrons during the chemical combination or bond formation to attain stable configuration of the nearest inert gas.

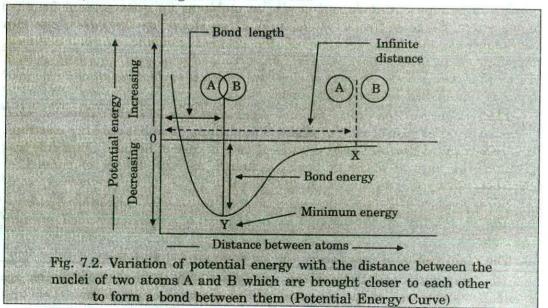
(*iii*) Atoms combine chemically as a result of transferring of electrons from the outer-most shell of one atom to that of the other or by sharing one, two or three electron pairs between the valence-shell of both the combining atoms. The transfer of electrons or sharing of electron pairs gives a stable configuration of 8 electrons to the valence-shell of both the atoms.

(iv) The tendency of an atom for transference or sharing its electron pairs is a measure of its chemical activity.

**3. Lowering of energy of combining atoms.** When two atoms combine together to form a bond, there is an over all decrease in the potential energy of the combining atoms, *i.e.*, a system having bonded atoms has lower energy than that having the unbonded atoms. This implies that the system of bonded atoms having lower energy is more stable than that of unbonded atoms having higher energy. From this it, therefore, follows that the process of chemical bonding between the atoms decreases the energy of the combining atoms and gives rise to the formation of a system which has lower energy and hence has greater stability.

#### **Potential Energy Curve**

The curve given in Fig. 7.2 shows the variation of potential energy with the distance between the nuclei of two atoms A and B which are approaching closer to each other to form a bond between them. The trend of the curve from right to left should be observed. When the two atoms A and B are far away, say at an infinite distance, from each other, the attraction between them is zero and hence, by convention, the energy of each of the atoms in arbitrarily taken to be zero and for stable system it is negative. It is for this



reason that there, is no possibility of the formation of any bond between them. This situation has been represented by point X shown at the far end towards the right of the curve.

As the two atoms are brought closer to each other, *i.e.* as the distance between the atoms is decreased, the attractive forces between the electrons and the nucleus become more dominant than the repulsive forces operating between the electrons of the two atoms and hence the energy of the system goes on decreasing as shown by the downward trend of the curve. This decrease of energy continues till a certain minimum value shown by point Y in the curve is obtained. Now if the atoms are brought still closer together, the repulsive forces between the two nuclei at such small inter-nuclear distance (inter-nuclear distance between the nuclei of the two atoms) becomes dominant and hence the energy of the system starts increasing as shown by the upward trend of the curve.

Point Y which is the minimum of the curve has the following characteristics: (a) At this point the attractive and repulsive forces are in equilibrium and hence a bond is said to be established between the atoms at this point.

(b) The overlapping between the orbitals of the two atoms is maximum at this point.

(c) The energy of the system at this point is minimum and hence AB molecule is in the stablest position. The inter-nuclear distance is also minimum at this point. The minimum energy value and inter nuclear distance corresponding to this point are called respectively *bond energy* and *bond length* of AB molecule. For H<sub>2</sub> molecule the bond energy is 103.2 kcal/mole and bond length is 0.74Å.

The above description makes it evident that a chemical bond is formed between the two atoms when the potential energy of the combining atoms is minimum and when they are at the minimum distance from each other. In order to break the bond between the atoms as much energy has to be put in as was earlier lost in the formation of the bond. The amount of energy lost in the process of bond formation or needed to break the bond is a measure of the strength of the bond. More the energy decreased during bond formation (or combination of atoms in a molecule), the stronger is the bond between the atoms.

## **How Do Atoms Combine ?**

The process by which the atoms of the elements rearrange their outer-most shell electrons to get eight-electron outer-most shell configuration which is a stable configuration takes place in the following ways :

(i) In this way the transfer of one or more electrons from the valence-shell of an atom to the valence-shell of another atom takes place (Formation of ionic bond).

(*ii*) In this way one, two or three electron pairs of the valence- shell of both the combining atoms are shared between them. The shared electron pairs may be contributed equally by both the atoms (*Formation of covalent bond*) or may be contributed by only one of the combining atoms (*Formation of co-ordinate bond*).

## (Types of Bonds

Corresponding to the above two ways by which the two atoms rearrange their outer-most shell electrons to get an eight-electron outer-most shell configuration, we have the following four types of bonds (or linkages) which hold the atoms together in a molecule.

(i) Ionic or Electrovalent Bond. This type of bond is established by the transfer of one or more valence electrons from one atom to the other.

(ii) Covalent Bond. This type of bond is established by the sharing of one, two or three electron pairs between the combining atoms. Each of the two bonded atoms contributes one electron to make the shared electron pair and has equal claim on the shared electron pair, *i.e.*, the resulting electron pair fills the outershell of both the atoms and thus both the atoms attain the stable configuration of the nearest inert gas.

(*iii*) Co-ordinate Bond. A covalent bond in which both electrons of the shared electron pair come from one of the two atoms is called a coordinate bond.

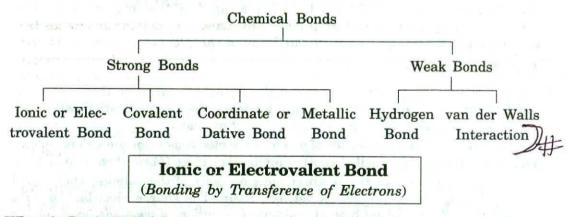
(*iv*) *Metallic Bond*. It is a typical bond and is formed in metals. In this bond a variable number of electrons are shared simultaneously by a variable number of atoms of the metal. This bond is altogether different from the three bonds mentioned above. This bond will be described in detail in subsequent pages of this chapter.

All these four bonds are called **strong bonds**. There are, however, attractive interactions between the atoms which are comparatively weaker than the bonds mentioned above. These weaker interactions are called **weaker bonds**. In these bonds the bonding atoms do not lose their identity. These weaker bonds are of the following types.

(i) Hydrogen Bond. This bond involves the bonding of a hydrogen atom with two strongly electronegative atoms (e.g. N, O and F) simultaneously.

(ii) van der Walls Interaction. This bond involves the interaction between atoms or molecules having inert gas configuration.

Thus the classification of bonds can be illustrated as follows :

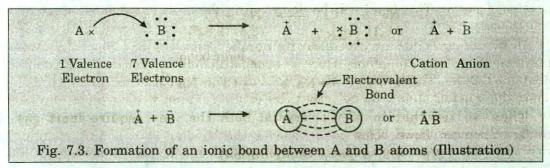


## What is Ionic Bond?

The chemical bond formed between two atoms by the transfer of one or more valence electrons from one atom to the other is called ionic bond. This bond is also called **electrovalent** or **polar bond**.

One of the combining atoms has excess of electrons than the stable number (2 or 8) in its valence-shell while the other atom is short of electrons and hence needs electrons to complete its octet. When they combine, the former surrenders surplus electrons to the latter and as a result of this transfer of electrons each of the atoms attains the stable configuration of the nearest inert gas (*i.e.*  $ns^2p^6$  configuration). The compounds which contain electrovalent bonds are called **electrovalent** or **ionic compounds**.

**Illustration of the formation of ionic bond.** How an ionic bond is established between two atoms can be explained by considering a general case in which an atom A forms an ionic bond with another atom B. Atom A has one electron in its valence-shell while atom B has seven electrons. Thus A has one electron in excess and B has one electron short than the stable octet. Therefore A transfers an electron to B and in this transaction both the atoms acquire a stable electronoctet. The resulting positive ion (cation), A<sup>+</sup> and negative ion (anion), B<sup>-</sup> are held together by electrostatic force of attraction which is called ionic bond or electrovalent bond. (See Fig. 7.3).



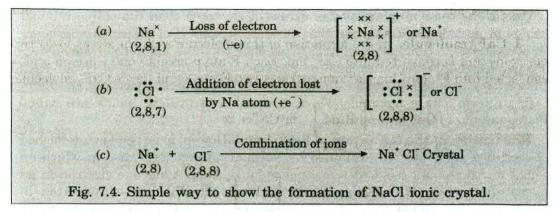
Thus an ionic bond can also be defined as the electrostatic force of attraction between cation and anion which are produced by the transfer of electrons.

## Examples of Ionic Compounds (NaCl, MgO, CaF<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>).

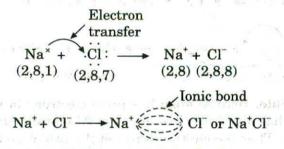
The symbol of an element surrounded by a number of dots (.) or crosses (x) equal to the number of valence electrons is called the *Lewis symbol* of the element. The structural formulae of molecules built by the union of Lewis symbols of the component atoms are called *electron-dot formulas* or *electron dot structures* or *Lewis structures*.

Now let us write the Lewis structure of some ionic compounds. **1. NaCl molecule.** Here Na (2, 8, 1) transfers its excess one electron to Cl atom (2, 8, 7) and thus Na atom acquires the configuration of Ne (2, 8) and Cl acquires the configuration of Ar (2, 8, 8).

The electron lost by Na atom is accepted by Cl atom and consequently Na atom is converted into a *positively charged ion* (*i.e. cation*) and Cl atom is converted into a *negatively charged ion* (*i.e. anion*). The two ions thus formed attract each other by electrostatic force of attraction which leads to the formation of an ionic or electro-valent bond between  $Na^+$  and  $Cl^-$  ions. Different steps are shown below in Fig 7.4



The formation of Na<sup>+</sup>Cl<sup>-</sup> ionic crystal shown by equations (a), (b), and (c) in Fig. 7.4 can also be depicted as :



Thus we see that in  $Na^+Cl^-$  crystal both the ions acquire inert gas configuration as shown below :

 $Na^+ \rightarrow 2, 8$  (Neon configuration)

 $Cl^- \rightarrow 2, 8, 8$  (Argon configuration)

The dots (  $\cdot$  ) and crosses (x) indicate the electrons in the outer-most shells of Cl and Na atoms.

2. MgO molecule. In the formation of this molecule Mg atom loses its two electrons from its outer-most shell (Mg  $\rightarrow$  2, 8, 2) which are taken up by oxygen atom (O  $\rightarrow$  2, 6). This converts Mg atom into Mg<sup>+2</sup> ion and O atom into O<sup>2-</sup> ion. The ions thus formed attract each other and form MgO molecule.

$$Mg : \xrightarrow{-2e^{-}} \left[ : \overset{\cdot}{Mg} : \right]^{2+} or Mg^{2+} + 2e^{-}$$

$$(2, 8, 2) \qquad (2, 8)$$

$$: \overset{\cdot}{O} : + 2e^{-} (From Mg atom) \longrightarrow \left[ : \overset{\cdot}{O} : \right]^{2-} or O^{2-}$$

$$(2, 6) \qquad (2, 8)$$

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

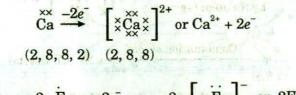
$$(2, 8) (2, 8)$$

$$or Mg(\overset{\cdot}{X}) + \overset{\cdot}{O} : \longrightarrow Mg^{2+} + O^{2-} or Mg^{2+} O^{2-}$$

$$(2, 8, 2) \quad (2, 6) \qquad (2, 8) (2, 8)$$

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**3.**  $CaF_2$  molecule. In the formation of this molecule each Ca atoms loses two electrons and is converted into  $Ca^{2+}$  ion. Each F atom accepts one electron and is converted into  $F^-$  ion. One  $Ca^{2+}$  ion attracts two  $F^-$  ions and forms  $CaF_2$  molecule.



$$2:F: +2e \longrightarrow 2 [:F:] \text{ or } 2F$$

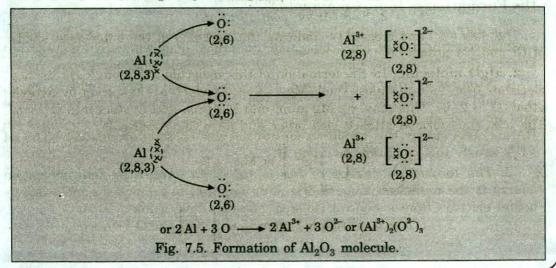
$$(2,7) \qquad (2,8)$$

$$Ca^{2+} + 2F \longrightarrow F Ca^{2+} F \text{ or } Ca^{2+} 2F \text{ or } Ca^{2+} F_2^{-}$$

$$or Ca^{*} + F \text{ or } Ca^{2+} F \text{ or } Ca^{2+} F \text{ or } Ca^{2+} F$$

(2,8,8,2) (2,7) (2,7) (2,8,8) (2,8) (2,8) (2,8)

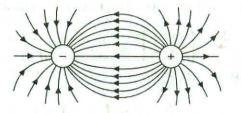
<sup>Al</sup> (4. Al<sub>2</sub>O<sub>3</sub> molecule. Here Al atom has three electrons in its valence shell (2, 8, 3) while oxygen has six (2, 6). Two atoms of Al transfer their six electrons to three oxygen atoms. Thus the electron-octets of the two Al and three O atoms are achieved. The two Al atoms deprived of three electrons each, give two Al<sup>3+</sup> ions while the three O atoms having gained two electrons each, give three  $O^{2-}$  ions. In this way we get  $Al_2^{3+} O_3^{2-}$  or  $Al_2O_3$  molecule (See Fig. 7.5).



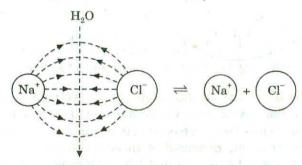
#### **Nature of Ionic Bond**

When two oppositely charged ions combine together, they attract each other by electrostatic force of attraction and are thus held together by the lines of force of attraction.

Since an ion can attract other ions having opposite charge on them from any direction, ionic bond is non-directional in nature and extends equally in all *directions*. If the ions are regarded as charged spheres, the attraction between the ions having opposite charge can be shown as follows :



When an ionic compound is dissolved in water, the lines of force of attraction holding the ions together are broken by the high dielectric constant value of water and thus the ions constituting the ionic compound are separated from each other as shown below for Na<sup>+</sup>Cl<sup>-</sup> ionic crystal.



# Factors Favouring the Formation of Ionic Compounds : Conditions for the Formation of Ionic Compounds

The formation and the stability of the ionic compounds depend on how easily the ions constituting the ionic compound are formed. Following are the important factors which favour the formation of ions (*i.e.* of ionic compounds) :

1. Number of valence electrons. The atom A which is converted into cation,  $A^+$  should possess 1, 2 or 3 valence electrons while the atom B which is converted into anion,  $B^-$  should have 5, 6 or 7 valence electrons. The element of groups IA, IIA and IIIA satisfy this condition for atom A and those of groups VA, VIA and VIIA satisfy this condition for atom B.

**2.** The ionisation energy of the metal atom should be low. Ionisation energy is the minimum amount of energy required to remove the most loosely bound electron from a neutral isolated gaseous atom. Thus :

Quite obviously if an atom has low ionisation energy, it will be easy for it to lose the electron and hence get converted into a cation. Hence low ionisation energy of the metal will favour the formation of cation.

3. Electron affinity of the non-metal should be high. Electron affinity is the amount of energy released when an electron is added to a neutral isolated gaseous atom. Thus :

 $\begin{array}{ccc} B \ (g) + e^- \rightarrow B^- \ (g) + Energy \ released \ (Electron \ affinity) \\ Gaseous & Anion \\ neutral \\ atom \end{array}$ 

Now, since the release of energy is the sign of stability of a system, the atoms with high electron affinity will form the anions quite easily.

4. The lattice energy of the ionic compound formed should be high. The energy released when one gram mole of a crystal is formed from its gaseous ions is called the lattice energy of the crystal. Thus :

 $A^+(g) + B^-(g) \rightarrow A^+ B^-(crystal) + Energy released (Lattice energy)$ 1 mole 1 mole 1 mole

Higher the value of lattice energy of a crystal, the greater is the ease of its formation, i.e., greater will be the stability of the ionic crystal.

The energy released in the formation of ionic molecule,  $A^+ B^-$  will lower the energy of the system, *i.e.*, for the formation of stable ionic compound there must be a net lowering of the energy.

For lattice energy to have a high value, the electrostatic force of attraction between the constituent ions of the ionic compound should be high. According to Coulomb's law the force of attraction (F) between two oppositely charged ions in air with charges equal to  $q_1$  and  $q_2$  and separated by a distance equal to d is given by:

$$\sqrt{r} = \frac{q_1 q_2}{d^2} = \frac{q_1 q_2}{(r_A^+ + r_B^-)^2}$$

d is equal to the sum of the radii of the positive and negative ions. From this relation it is clear that to have a large value of force of attraction (or lattice energy) the following two condition should be satisfied.

(a) The electric charges on the ions (i.e.  $q_1$  and  $q_2$ ) should be large. For example the force of attraction between the doubly-charged Mg<sup>2+</sup> ion and the doubly-charged O<sup>2-</sup> ion in Mg<sup>2+</sup> O<sup>2-</sup> ionic crystal is 4 times greater than that between monovalent Na<sup>+</sup> and Cl<sup>-</sup> ions in Na<sup>+</sup> Cl<sup>-</sup> crystal. Here it has been assumed that the distance between the ions in both the ionic compounds is the same. Consequently MgO is more stable than NaCl.

(b) d or  $(r_A^+ + r_B^-)$  should be small, i.e., the cation and the anion constituting the ionic compound should be small in size. Thus for a given anion, the smaller the radius of the cation, the greater is the strength of the ionic bond, *i.e.* greater is the stability of the ionic crystal. For example, since Na<sup>+</sup> ion is smaller than Cs<sup>+</sup> ion, the force of attraction between Na<sup>+</sup> and Cl<sup>-</sup> ions in Na<sup>+</sup> Cl<sup>-</sup> ionic crystal is more than that between Cs<sup>+</sup> and Cl<sup>-</sup> ions in Cs<sup>+</sup> Cl<sup>-</sup> ionic crystal. Thus the lattice energy of Na<sup>+</sup> Cl<sup>-</sup> is higher than that of Cs<sup>+</sup>Cl<sup>-</sup>. Consequently Na<sup>+</sup>Cl<sup>-</sup> compound will be formed more easily than Cs<sup>+</sup> Cl<sup>-</sup> compound. In other words Na<sup>+</sup>Cl<sup>-</sup> is more stable than Cs<sup>+</sup> Cl<sup>-</sup>.

Similarly, for a given cation, the smaller the radius of the anion, the greater is the strength of the ionic bond, *i.e.*, the greater is the stability of the ionic compound.

5. Electronegativity difference of A and B should be high. From the line of arguments used in 2nd, 3rd, and 4th conditions discussed above, we can say that atoms A and B will form an ionic bond, if they have greatly different electronegativities. In fact, a difference of 2 or more is necessary for the formation of an ionic bond between atoms A and B. For example, since the electronegativity difference between Na and Cl is 2.1 (Na = 0.9, Cl = 3.0), Na and Cl will form an ionic bond in NaCl molecule.

#### Formation of Ionic Bonding and Periodic Table

The relative tendency of the atoms to turn into cations and anions depends on their position in the periodic table. The elements having *low ionisation energies*, *i.e., elements of groups IA and IIA have a strong tendency to turn into cations*. The elements having *high electron affinities*, *i.e., the higher elements of groups* VA and VIA and those of group VIIA, have a strong tendency to turn into anions.

Thus the binary compounds having ionic bonding are most readily formed by the elements of groups IA and IIA with oxygen (group VIA) and halogens (VIIA group) elements.

#### Electrovalency

Electrovalency of an element is its combining capacity in an ionic compound, *i.e.*, when an element forms electrovalent bond, its valence is known as its electrovalency. Electrovalency of an element is equal to the number of electrons lost by an atom of that element in forming a positive ion or gained by it in forming a negative ion, both having the noble gas configuration ( $s^2p^6$  configuration) in their outermost shell. The elements which lose electrons show positive electrovalency. For example in the formation of NaCl the electrovalency of Na is equal to +1 while that of Cl is equal to -1. An element which gains or loses one, two, three, four ... etc. electrons is called mono (or uni) valent, di (or bi) valent, trivalent, tetravalent etc. ... element. Examples are :

Na, Cl, F	Monovalent elements
Mg, Ca, O	Divalent elements
Al, B,	Trivalent elements
C, Si	Tetravalent elements

# Variable Electrovalency

There are many elements which show different values of electrovalency in different electrovalent compounds. This phenomenon is called *variable* electrovalency which is due to the following two reasons (i) Unstable configuration of the core or kernel, and (ii) Inert electron pair effect.

1. Unstable configuration of the core. The outermost levels of the elements like Fe, Co, Ni, Cu etc. contain only one or two electrons. When these electrons are lost, the remaining part which is called the *core* or *kernel*, is unstable and hence some more electrons from the core can be further lost, giving variable electrovalency to the ion. For example :

(a) The variable electrovalency of iron equal to + 2 in ferrous compounds and equal to +3 in ferric compounds can be explained as follows :

Fe (26)  $\rightarrow 2$ , 8, 14, 2 or 2, 8,  $3s^2p^6d^6$ ,  $4s^2$ 

 $Fe^{2+}$  (24)  $\rightarrow 2, 8, 14, \text{ or } 2, 8, 3s^2p^6d^6$  and also also also also be a side of the second seco

 $3s^2p^6d^6$  configuration is unstable and hence loses one more electron and thus forms Fe<sup>3+</sup> ion investory 'the other by manual harding of the and and

 $Fe^{3+}$  (23)  $\rightarrow 2, 8, 13, \text{ or } 2, 8, 3s^2p^6d^5$ 

(b) An increase in the nuclear charge tends to prevent the removal of electrons from a lower energy level. For example Co (Z = 27) atom forms  $Co^{3+}$  ion with great difficulty because 3d electrons are more firmly retained by cobalt nucleus with positive charge equal to +27 which is one unit higher than that on iron nucleus (= + 26)

> $Co (27) \rightarrow 2, 8, 15, 2 \text{ or } 2, 8, 3s^2p^6d^7, 4s^2$  $Co^{2+}$  (25)  $\rightarrow 2$ , 8, 15 or 2, 8,  $3s^2p^6d^7$  $Co^{3+}$  (24)  $\rightarrow 2, 8, 14$  or 4, 8,  $3s^2p^6d^6$ Olygin, Distancianticut concept of

(c) The variable electrovalency of Cu equal to +1 (cuprous ion) and +2 (cupric ion) is easily understood from the electronic configurations given below :

> $Cu (29) \rightarrow 2, 8, 18, 1 \text{ or } 2, 8, 3s^2p^6d^{10}, 4s^1$  $Cu^+$  (28)  $\rightarrow$  8, 8, 18 or 2, 8,  $3s^2p^6d^{10}$  $Cu^{2+}(27) \rightarrow 2, 8, 17$  or 2, 8,  $3s^2p^6d^9$

2. Inert electron pair effect. Some of the heavier elements of p-block of the long form of periodic table like those of groups IIIA (Ga, In, Tl), IVA (Ge, Sn, Pb), VA (As, Sb, Bi) and VI A (Te Po) show two oxidation states (i.e. electrovalencies) as shown below :

Group IIIA (G = 3)  $\rightarrow$  Ga (+1, +3), In (+1, +3), Ti (+1, +3) Group IVA (G = 4)  $\rightarrow$  Ge (+2, +4), Sn (+2, +4), Pb (+2, +4) Group VA (G = 5)  $\rightarrow$  As (+3, +5) Sb (+3, +5), Bi (+3, +5) Group VIA (G = 6)  $\rightarrow$  Te (+4, +6), Po (+2, +4)

These two oxidation states differ from each other by two units. The higher oxidation state for most of the elements is equal to their group number, G while the lower ones are equal to (G-2) as shown above. Group number oxidation state (= G) is obtained when all the ns and np electrons from  $ns^2p^x$  configuration of p-block elements (x = 1, 2, 3 and 4 for the elements of groups IIIA, IVA, VA and VIA respectively) are lost while the lower oxidation state is obtained when only np electrons are lost and the ns electron pair, due to its extra stability, remains inert, i.e., it is not lost. Such a pair of ns electrons is called inert electron pair and the effect caused by it is called inert electron pair effect.

The inert electron pair effect has been used to explain the electrovalencies of the elements given above.

#### Formation of an Ionic Bond also Involves Decrease in Energy

As a general rule, the formation of an ionic bond also involves a decrease in energy. This fact can be illustrated by considering the formation of one gm molecule of solid sodium chloride, NaCl (s) through the following steps :

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1. Conversion of Na atom from the solid state to the gaseous state [Na (s)  $\rightarrow$  Na (g)]. This type of conversion is called sublimation of solid sodium into gaseous sodium. Since in the solid state Na atoms are fairly close to each other while in the gaseous state they are relatively far apart, the conversion of Na(s) into Na(g) requires the absorption of energy, *i.e.*, this conversion is an endothermic reaction. The energy required to convert one mole of Na(s) to Na(g) is called sublimation energy which has been found to be equal to 108.81 kJ/mole. Energy absorbed in the reaction is shown at the left hand side of the equation.

Na(s) + Sublimation energy (= 108.81 kJ. mole<sup>-1</sup>)  $\rightarrow$  Na (g)

(Endothermic reaction)

**2.** Dissociation of  $\operatorname{Cl}_2(g)$  molecules into  $\operatorname{Cl}(g)$  atoms  $[\frac{1}{2}\operatorname{Cl}_2(g) \to \operatorname{Cl}(g)]$ . Here, again, energy is to be supplied in order to break the bond between two Cl atoms in  $\operatorname{Cl}_2$  molecule (Cl–Cl bond). In this step half a molecule of  $\operatorname{Cl}_2(g)$  absorbs energy equal to half of the dissociation energy of  $\operatorname{Cl}_2(g)$  and is converted into  $\operatorname{Cl}(g)$ . Dissociation energy of  $\operatorname{Cl}_2(g)$  has been found equal to 242.7 kJ/mole. Absorption of energy means that the process is an endothermic reaction. Thus :

3. Removal of an electron from gaseous Na atom  $[Na(g)-e^- \rightarrow Na^+(g)]$ . The removal of an electron from gaseous Na atom requires energy equal to the *ionisation energy* of Na. Thus the removal of an electron from Na (g) is an *endothermic reaction*. Ionisation energy of sodium is equal to 495.8 kJ/mole. Thus :

Na (g) + Ionisation energy (495.8 kJ/mole)  $\rightarrow$  Na<sup>+</sup>(g) + e<sup>-</sup>

(Endothermic reaction).

4. Conversion of Cl(g) atom into  $Cl^{-}(g)$  ion  $[(Cl(g) + e^{-} \rightarrow Cl^{-}(g)]$ . Here Cl(g) atom adds the electron given by Na(g) atom in step (3) to form  $Cl^{-}(g)$ . In this process Cl(g) releases energy equal to its electron affinity (or affinity energy) which is equal to 348.7 kJ/mole. The energy released is shown at the right hand side of the equation. The release of energy means that the conversion of Cl(g) to  $Cl^{-}(g)$  is an exothermic reaction. Thus :

Cl (g) +  $e^- \rightarrow Cl^-$  (g) + Affinity energy (= 348.7 kJ/mole)

(Exothermic reaction).

5. Combination of  $Na^+(g)$  and  $Cl^-(g)$  ions to form NaCl (s)  $[Na^+(g) + Cl^-(g) \rightarrow NaCl$  (s)]. This is the final step in which  $Na^+(g)$  and  $Cl^-(g)$  ions formed in steps (3) and (4) respectively combine together to form one mole of solid sodium chloride crystal, NaCl (s). Here attractive forces between  $Na^+(g)$  and  $Cl^-(g)$  operate and thereby decrease the energy of the system. Thus the formation of NaCl (s) from the combination of  $Na^+(g)$  and  $Cl^-(g)$  is accompanied by the release of energy. The energy released is called *lattice energy* of NaCl which has been found (for NaCl) to be equal to 769.2 kJ/mole. Thus :

 $Na^{+}(g) + Cl^{-}(g) \rightarrow NaCl(s) + Lattice energy (= 769.2 \text{ kJ/mole})$ 

(Exothermic reaction).

Now,

Total energy absorbed = 108.81 + 121.35 + 495.80 = 725.96 kJ. and, Total energy released = 348.7 + 769.2 = 1117.9 kJ.

Since total energy released is larger than the total energy absorbed, in the formation of NaCl ionic crystal energy is released and its magnitude is equal to 1117.90 -725.96 = 391.94 kJ. Thus we see that the net process of the formation of NaCl crystal by the transfer of an electron from Na atom to Cl atom involves the evolution of energy. Hence the formation of ionic bond between Na<sup>+</sup> and Cl<sup>-</sup> ions of NaCl(s) ionic crystal involves decrease in energy. The release of energy in the formation of an ionic bond in NaCl solid also shows that the ionic bond is a very strong bond.

#### Properties of Ionic Compounds

1. **Physical state.** Ionic compounds consist of three dimensional solid aggregates of cations and anions which are arranged in a well-defined geometrical pattern. Thus ionic compounds are *crystalline solids* at room temperature. They are never liquids or gases under the ordinary conditions of temperature and pressure, since their ions lack the freedom of movement characteristic of the liquid or gaseous state.

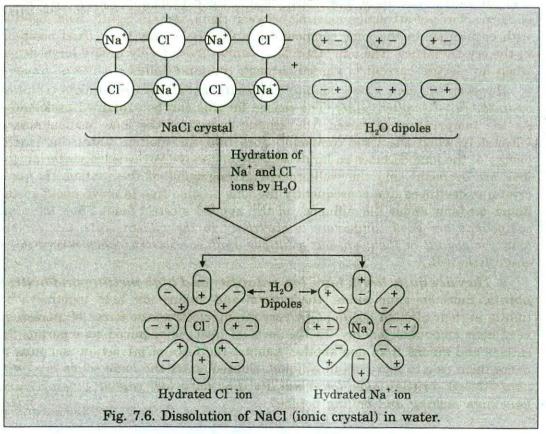
2. Electrical conductivity. Ionic compounds do not conduct electricity when they are in the solid state. The reason is that the cations and anions, on account of electric force of attraction existing between them, remain tightly held together with each other in the ionic compounds and hence occupy their fixed positions in the crystal lattice. The ions, therefore, cannot move freely to any large extent when an electric current is passed through the ionic solids.

However, the ionic solids conduct electricity when they are in water solution or in the fused (molten) state. The reason for this can be explained as follows : As the temperature is raised, the kinetic energy of the ions also increases. Ultimately when the ionic compound goes into the molten state, the kinetic energy of the ions becomes so large that the attractive forces acting between the ions are overcome and the well-ordered arrangement of the ions in the ionic crystal is destroyed and consequently the ions become free to move about in the liquid medium under the influence of the applied electric field. Thus the ionic compounds are good conductors of electricity in the molten state, i.e., molten ionic compounds or their aqueous solutions conduct a current when placed in an electrolytic cell.

3. They are quite hard, have low volatility and high melting and boiling points. Since in ionic solids, the cations and anions are held together very tightly in their allotted positions by very strong electrostatic forces of attraction, very high amount of energy (in the form of heat) is required to separate the cations and anions from one another against the force of attraction and thus to make them free to move, as in a liquid. Consequently the ionic solids are quite hard (though brittle), have low volatility (i.e., have low vapour pressure) and have high melting and boiling points.

4. Solubility in polar and non-polar solvents. Ionic solids are freely soluble in polar solvents like  $H_2O$ , liq.  $NH_3$  etc., because the electrostatic force of attraction holding the cations and anions together in the ionic solids is reduced by the high value of dielectric constant of the polar solvent. The reduction in the electrostatic force of attraction by the high dielectric constant value of polar solvent makes the ions move freely and interact with solvent molecules to form the solvated ions. On the other hand ionic solids are insoluble or slightly soluble in non-polar solvents (organic solvents) such as  $C_6H_6$ ,  $CCl_4$  etc. Such solvents, due to their low value of dielectric constant, do not allow the ions to move freely and interact with them to form the solvated ions.

The solubility of ionic solids in a polar solvent like water can also be explained by saying that a water molecule is a dipole and hence the positive end of water dipole interacts with the negative ion of the ionic solids and the negative end of the dipole interacts with the positive ion of the same ionic crystal as shown in Fig. 7.6 in which the dissolution of NaCl ionic crystal in water has been shown. The interaction between the water dipoles and the ions of the crystal lowers down the energy of the system and thus the force of attraction between the cations and anions of the ionic solid is weakened. Consequently the water molecules tear off the ions from the crystal lattice and make them float in the bulk of water. Further, they are surrounded by water dipoles with the oppositely charged ends directed towards them (See Fig. 7.6).



**Explanation of dissolution on the basis of relative magnitutes of lattice** and hydration energies. The dissolution of an ionic compound in a polar solvent can also be explained on the basis of relative values of lattice and hydration energies. The dissolution of an ionic compound in a polar solvent takes place through the following two steps :

Step (a). When an ionic solid, MX(s) is dissolved in a polar solvent, the ionic solid is broken into its isolated gaseous ions viz.  $M^+(g)$  and  $X^-(g)$ . In this process of breaking, some amount of energy is required. This is called **lattice energy** of MX(s) ionic crystal. Thus :

 $\begin{array}{c} \text{MX}(s) + \textit{Energy required (called lattice energy)} \rightarrow \underbrace{\text{M}^+(g) + \text{X}^-(g)}_{\text{Isolated gaseous}} \end{array}$ 

Step (b). In this step the isolated gaseous ions formed in step (a) go into the solvent and interact with their molecules so that they get surrounded by a definite, but unknown, number of solvent molecules and are consequently converted into solvated ions which are represented as  $[M(solv)_x]^+$  and  $[X(solv)_y]^-$ . Here solv stands to show solvent molecules. The formation of these solvated ions is due to the *ion-solvent interaction*. If water is used as a solvent, the gaseous ions are said to be converted into **hydrated ions** which are represented as  $[M(H_2O)_x]^+$  or  $[M(aq)]^+$  and  $[(X(H_2O)_y]^-$  or  $[X(aq)]^-$ . This representation of hydrated ions indicates that the ions are in aqueous phase. The process by which the solvated (or hydrated) ions are produced is called solvation (or hydration) process. The process of solvation (or hydration) is accompanied by the release of a certain amount of energy which is called **salvation** (or **hydration**) energy.

 $M^+(g) + x(solv) \rightarrow [M (solv)_x]^+ + Energy released (called solvation energy) Solvated cation$ 

 $X^{-}(g) + y(solv) \rightarrow [X(solv)]^{-} + Energy released (called solvation energy) Solvated anion$ 

Thus the amount of energy released when one gm mole of a gaseous ion is dissolved in a solvent (or water) is called solvation (or hydration) energy of the solvent. Solvation (or hydration) energy is also called heat of solvation (or heat of hydration). Obviously the process of solvation (or hydration) is an exothermic process.

Now for an ionic solid to dissolve in a polar solvent, the magnitude of hydration energy of the solvent should be such that it should be able to overcome (*i.e.* offset, counteract or break down) the lattice energy of the ionic solid which is responsible for holding the ions together in the ionic crystal. Thus for an ionic solid to dissolve in a polar solvent, the solvation energy of the solvent must be greater than the lattice energy of the ionic solid so that the solvation energy may overcome the lattice energy.

When we consider the possibility of the solubility of ionic solids in non-polar solvents, we find that the non-polar solvents are not able to interact with the gaseous ions to form the solvated ions and hence no energy is released in the form of solvation energy which may break down the lattice energy. Thus ionic solids are not soluble in non-polar solvents.

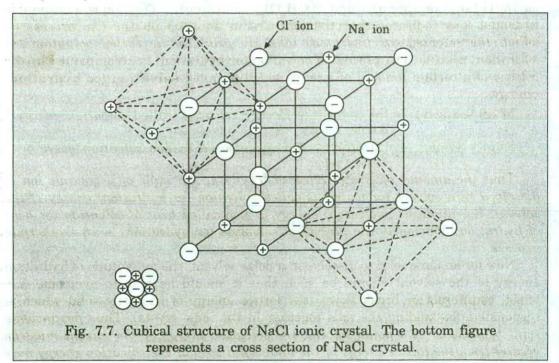
ions

**5.** Stability. Ionic crystals are very stable compounds and for maximum stability of these crystals the oppositively charged ions are close to one another and the similarly charged ions are as away from one another as possible.

**6.** Crystal structure (Packing of ions in ionic crystals). Single ionic molecules  $(e.g. \operatorname{Na^+Cl^-})$  do not exist as such in the solid form of ionic compounds, *i.e.*, ionic solids do not exist as individual neutral independent molecules. Rather, a number of cations and anions attract each other due to electrostatic force of attraction which is nondirectional and hence extends in all directions. In order to occupy minimum space the ions arrange themselves systematically in an alternating cation-anion pattern called **crystal** or **lattice**. Thus we see that *ionic solids consist of three dimensional solid aggregates*.

The structure (*i.e.* geometry) of an ionic crystal depends on radius ratio of the cation and anion  $(r_c^+/r_a^- \text{ ratio})$ . For example CsF has the same structure as NaCl, since both the ionic molecules have the same radius ratio.

Ionic crystals possess typical structure of their own. In each type of the structure of an ionic crystal each ion of one type is surrounded by a certain number of ions of opposite charge equidistant form it. The structure of NaCl ionic crystal can be considered as an example. It has *cubical* shape (Fig. 7.7). X-ray study of the structure of this ionic crystal has shown that :



(a) The distance between two adjacent ions of the same kind like, say Cl<sup>-</sup> ions (*i.e.*, length of the edge), is equal to 5.63 Å while the distance between the two adjacent ions of different kind like, say Na<sup>+</sup> and Cl<sup>-</sup> ions, is equal to 5.63/2 = 2.815 Å.

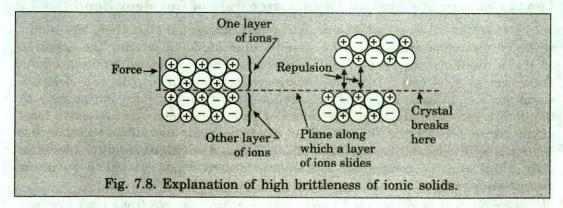
(b) Na<sup>+</sup> and Cl<sup>-</sup> ions are so located that each Na<sup>+</sup> ion is surrounded by equally spaced six Cl<sup>-</sup> ions placed at the corners of a regular octahedron and similarly each Cl<sup>-</sup> ion is surrounded by equally spaced six Na<sup>+</sup> ions placed at the corners of an octahedron (See Fig. 7.7). Thus the coordination number of each ion is six and NaCl crystal has octahedral structure. In other words, NaCl structure has 6 : 6 coordination.

It is worth noting that  $Na^+$  and  $Cl^-$  ions are not connected to one another by pairs, since all the six  $Cl^-$  ions are the same distance away from any one  $Na^+$ ion. Thus for maximum stability of NaCl crystal the oppositely charged ions are close to one another and the similarly charged ions are as away from one another as possible.

Although discrete molecules (Na<sup>+</sup>Cl<sup>-</sup>) do not exist in the solid from of ionic crystals, independent molecules do exist in the vapour form of ionic compounds.

7. Highly brittle. Ionic solids are highly brittle, *i.e.*, if a little external force is applied on ionic crystals, they are generally easily broken. This property is called brittleness and can be explained as follows :

We know that ionic solids are composed of parallel layers which contain cations and anions in alternate positions so that the opposite ions in the various parallel layers lie over each other. When a little external force is applied on an ionic crystal, one layer of ions slides a bit over the other layer along a plane. The sliding of a layer over the other results in that the like ions come in front of each other and hence begin to repell each other (Fig. 7.8). Consequently the application of a little external force brings about repulsion between the two layers and the ionic solid breaks. Hence ionic solids are highly brittle.



8. High density. The electrostatic force of attraction existing between the cations and anions in an ionic crystal brings these ions very close to one another. This decreases the volume of the crystal and consequently the ionic crystals have high density.

**9.** They undergo ionic reactions. The reactions of an ionic compound are precisely the reactions of its constituent ions. Such reactions which are called *ionic reactions* take place as a result of collision between cations and anions, giving rise to the formation of new ionic compounds. Ionic reactions are practically

rapid and instaneous (i.e. precipitation). For example  $Cl^-$  ions present in NaCl give white precipitate of AgCl as soon as AgNO<sub>3</sub> solution is added to that of NaCl.

10. They show isomorphism. Ionic solids made up of ions with identical electronic configurations show an identity of crystalline form which is called *isomorphism*. Two such pairs of isomorphous compounds are (a) NaF and MgO, and (b) CaCl<sub>2</sub> and K<sub>2</sub>S.

(a)	Sodium	fluoride	and	Magnessium	oxide
	Na <sup>+</sup>	$\mathbf{F}^{-}$		$\mathrm{Mg}^{2+}$	O <sup>2–</sup>
	(2, 8)	(2, 8)		(2, 8)	(2, 8)
<i>(b)</i>	Calcium	chloride	and	Potassium	sulphide
	Cl-	Ca <sup>2+</sup> Cl <sup>-</sup>		$K^{+}$ $S^{2-}$	$K^+$
	(2, 8, 8)	(2, 8, 8) $(2, 8, 8)$		(2, 8, 8) (2, 8, 8)	(2, 8, 8)

11. They do not exhibit isomerism. Ionic bond involving electrostatic lines of force between opposite ions is non-rigid and non-directional. The ionic compounds are, therefore, incapable of exhibiting stereoisomerism.

## **Covalent Bond**

(Bonding by Mutual Sharing of Electrons)

## Lewis Concept of Covalent Bond: Octet Rule of Covalent Bond

In 1916 G.N. Lewis, an American chemist, suggested that there are atoms which can combine with each other or with other atoms by sharing the unpaired electrons in their outermost shells. In this way the occupied orbitals of the outermost shell of each of the participating atoms are filled with two electrons which have opposite spins. Consequently *the paired electrons are shared by both the atoms* and circulate about the nuclei of both the atoms. The attractive force of the two nuclei for the shared pair of electrons holds the atoms together and gives rise to the formation of a bond which is called **covalent bond** or **electron pair bond** and the compounds containing covalent bonds are called **covalent compounds.** Thus :

(The chemical bond between two atoms in which the electrons (in pairs) are shared by both the participating atoms is called covalent bond.)

Each of the two combining atoms contributes one electron to the electron pair and has equal claim on the shared electron pair.

According to Lewis concept when two atoms form a covalent bond between them, each of the atoms attains the stable configuration of the nearest inert gas, by completing its *octet* (*i.e.* 8 electrons in the outermost shell) or *duplet* (*i.e.* 2 electrons in case of hydrogen). The covalent bond is established between the atoms of the same or different elements. Since a covalent bond between atoms

results by the interaction of their electrons which become common to both the atoms, it is also called an **atomic bond**.

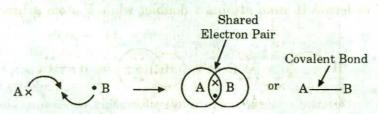
## Types of Covalent Bond (Single, double and triple covalent bonds).

The covalent bond formed by the sharing of one, two or three electron pairs between the participating atoms is called *single*, *double* and *triple covalent bond* respectively. These bonds are represented as follows :

Type of bond	Represented by	No. of electron pairs involved	Examples
Single covalent	Single dash	1 pair = 1 × 2	H–H, Cl–Cl,
bond	(–)	= 2 electrons	H–Cl, H–O–H
Double covalent	Double dash (=)	$2 pairs = 2 \times 2$ $= 4 electrons$	0 = 0
Triple covalent	Triple dash	3 pairs = 3 × 2	$N \equiv N$
bond	(≡)	= 6 electrons	

Double and triple covalent bonds are called multiple covalent bonds.

**Illustration of the formation of covalent bond.** How a covalent bond is formed between two atoms can be understood by considering a general case in which an atom A has one valence electron and another atom B has seven valence electrons. As these atoms approach nearer to each other, each atom contributes one electron and the resulting electron pair fills the outer shell of both the atoms. Thus atom A acquires 2 electrons and B, 8 electrons in their respective outer shells and the shared electron pair constitutes a covalent bond between A and B.



Writing the Electronic Formulae (Lewis Formulae) for Covalent Compounds  $(H_2, F_2, HF, H_2O, H_2S, NH_3, BF_3, CH_4, O_2, N_2, CO_2, C_2H_4, C_2H_2)$ .

The method used for writing the electronic formulae of covalent compounds consists of the following steps :

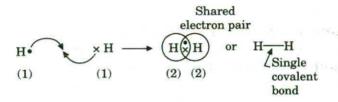
(a) Around the symbol of each atom in the formula, we place dots, crosses etc. equal to the number of electrons present in the valence-shell of the atom.

(b) The shared pair of electrons are indicated by electron signs like dots  $(\cdot)$ , crosses (x) etc which are placed between the symbols of the atoms.

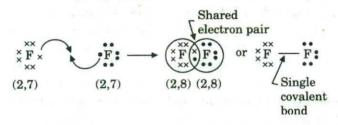
(c) Symbol of each atom and its octet is enclosed in a circle so that the two circles overlap the shared electrons. Thus each circle now has *eight* electrons (except *two* in case of H atom).

This method of writing the structure of covalent compounds can be illustrated by the following examples. For the differentiation of electrons, they have been shown by dots  $(\cdot)$  and crosses  $(\times)$ . The structures obtained are called **Lewis** structures or electron dot structures.

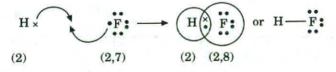
1.  $H_2$ ,  $F_2$  and HF molecules. (a)  $H_2$  molecule is composed of two H atoms, each having one valence electron. Each contributes an electron to the shared pair and both atoms acquire stable helium configuration. Thus stable  $H_2$  molecule results.



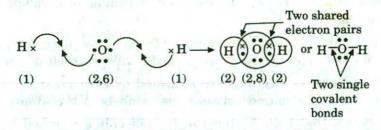
(b) In  $F_2$  molecule each F atom (2, 7) has seven valence electrons. The two F atoms achieve a stable electron octet by sharing a pair of electrons.



(c) In HF molecule H atom attains a doublet while F atom achieves an octet of electrons.

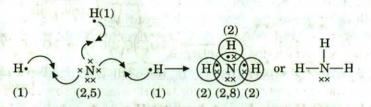


 $2/H_2O$  and  $H_2S$  molecules. (a) Oxygen atom (2, 6) has six valence electrons and achieves the stable octet by sharing two electrons, one with each H atom. Thus Lewis structure of water can be written as :



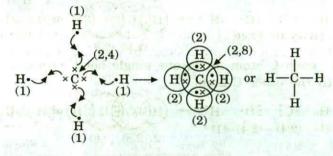
(b) On the same lines of argument Lewis structure of  $H_2S$  can also be written.  $(S \rightarrow 2, 8, 6)$ .

 $3/NH_3$  and  $BF_3$  molecules. (a) N atom (2, 5) has five valence electrons and can achieve the octet by sharing three electrons, one each with three H atoms. This gives the following Lewis structure to NH<sub>3</sub> molecule.

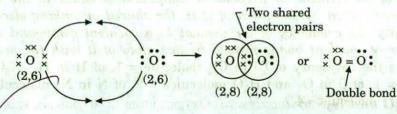


(b) On the same lines of agrument Lewis structure of BF<sub>3</sub> can also be written  $(B\rightarrow 2, 3, F\rightarrow 2, 7)$ .

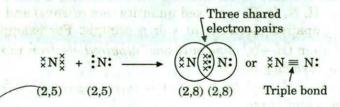
**4.** Methane molecule  $(CH_4)$ . Carbon atom (2, 4) has four electrons in the valence shell. It can achieve the stable octet by sharing these electrons with H atoms, one with each H atom. Thus the Lewis structure of  $CH_4$  can be written as :



**5**,  $O_2$  molecule. The conventional Lewis structure of  $O_2$  molecules is written by sharing two pairs of electrons between two O-atoms (2, 6). In this way both O-atoms achieve the octet and both O-atoms are linked by a double bond.

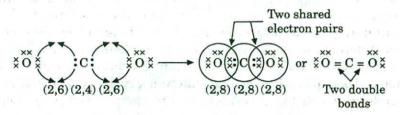


6.  $N_2$  molecule. The two N atoms (2, 5), each having five electrons in the valence shell, achieve the octet by sharing three electron pairs between them.

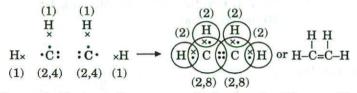


Thus we see that both N-atoms in  $N_2$  molecule are linked by a triple bond. **7.** CO<sub>2</sub> molecule. Carbon (2, 4) has four electrons in its valence-shell. It shares two electrons with each oxygen atom (2, 6). Thus C-atom and O-atom

both achieve their octet and carbon atom is linked with both O-atoms by a double bond.



8. Ethylene  $(C_2H_4)$  and acetylene  $(C_2H_4)$  molecules. (a) In  $C_2H_4$  each Catom achieves the stable octet by sharing its four electrons with two H-atoms and the other C atom. In this way each C-atom forms two single bonds with two H-atoms and one double bond with the other C-atom.



(b) In  $C_2H_2$ , each C-atom forms one single bond with one H-atom and one triple bond with the other C-atom.

$$\begin{array}{cccc} H_{\times} & \cdot C \vdots & \vdots C \cdot & \times H & \longrightarrow & H \end{array} & \begin{array}{c} H & c & \vdots & c & \times H \\ (1) & (2,4) & (2,4) & (1) \end{array} & \begin{array}{c} H & c & c & c & \times H \\ (2) & (2,8) & (2,8) & (2) \end{array} & \\ \hline \end{array}$$

The valency of an element in a covalent compound is called its covalency. Covalency of an element in a covalent compound is equal to the number of electrons contributed by one atom of it in the shared or linking electron pairs. Consequently, the covalency of an element in a covalent compound is equal to the number of covalent bonds formed by one atom of it with the neighbouring atom. Thus the covalency of Cl in Cl<sub>2</sub> molecule = 1, of H in H<sub>2</sub>, H<sub>2</sub>O and HCl molecules = 1, of O in O<sub>2</sub> and H<sub>2</sub>O molecules = 2, of N in N<sub>2</sub> molecule = 3, and of C in CH<sub>4</sub> molecule = 4.

#### Variable Covalency

Generally the covalency of an element which has only s and p orbitals in its valency-shell (e.g. H, N, O, F) is a fixed quantity (not always) and is equal to the total number of unpaired electrons in s or p orbitals. For example :

(i) Since H atom  $(H \rightarrow 1s^1)$  has only one unpaired electron in its orbital, this element shows a covaency of one.

(ii) N atom  $(N \rightarrow 2s^2, 2p_x^{1}, 2p_y^{1}, 2p_z^{1})$  has three unpaired electrons and hence exhibits a covalency of three.

(iii) O atom (O  $\rightarrow 2s^2$ ,  $2p_x^2$ ,  $2p_y^1$ ,  $2p_z^1$ ) which has two unpaired electrons shows a covalency of two.

(iv) F atom  $(2s^2, 2p_x^2, 2p_y^2, 2p_z^1)$  has one unpaired electron and, therefore, shows a covalency of one.

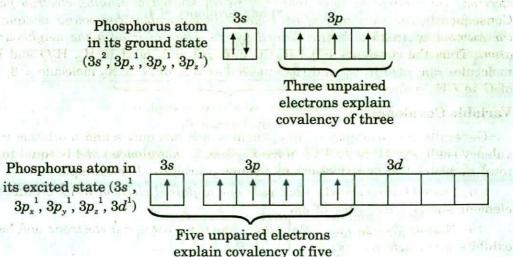
Note that the elements mentioned above have only s and p-orbitals in their valence-shells, *i.e.*, these elements do not contain vacant d-orbitals. However, the elements containing vacant d-orbitals (*e.g.* P, S, Cl etc.) show different values of covalency in different covalent compounds. This phenomenon is called *variable covalency* and is due to the presence of vacant d-orbitals in the valency-shell of these elements. Examples of elements, different covalencies shown by them and the compounds in which these covalencies are shown are given below :

Elements at coll solution	Different covalencies	Examples of compounds
Phosphorus	3	PCl <sub>3</sub>
511 AU9919	5 minutes	PCl <sub>5</sub>
Sulphur	2	$SCl_2$
and the second	P 14	$SF_4$
ally some after the terror of the	6	SF <sub>6</sub>
Halogen (other than	1	ICl
flourine)	3	ICl <sub>3</sub>
te one guora i cono no i i Piet re	5	IF <sub>5</sub>
	7	IF <sub>7</sub>

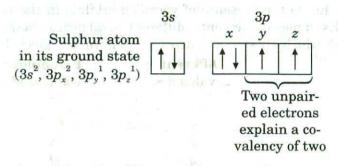
#### **Explanation of Variable Covalency**

Variable covalency of an element arises due to the increase in the number of unpaired electrons in the different excited states of the atom. For example the covalencies of P, S and Cl atoms can be explained as follows :

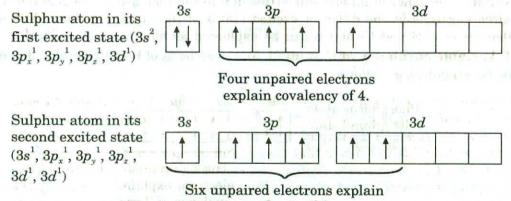
1. Variable covalency of P atom (3, 5). Covalencies of P atom equal to 3 and 5 can be explained as follows :



2. Variable covalency of S atom (2, 4, 6). (a) Covalency of 2. We know that the normal configuration of the valence shell of sulphur atom is  $3s^2$ ,  $3p_x^2$ ,  $3p_y^1$ ,  $3p_z^1$ . Sulphur atom having this configuration is said to be in the ground state and the configuration in this state is called ground state configuration. Thus normal configuration and ground state configuration is the same. The presence of two unpaired electrons explains a covalency of two for sulphur atom.

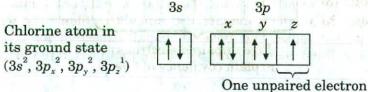


(b) Covalencies of 4 and 6. When sulphur atom forms covalent bonds with other atoms, energy is set free during the formation of these bonds and this energy makes one 3p electron or both 3s and 3p electrons jump to the vacant 3d-orbital. Now sulphur atom is said to be in the *excited state*. When only 3p electron jumps, we get *four* unpaired electrons which explain the covalency of 4 for sulphur atom. On the other hand when both 3s and 3p electrons jump, we get *six* unpaired electrons which account for the covalency of 6 for sulphur atom. How 4 and 6 covalencies of sulphur arise is shown below :

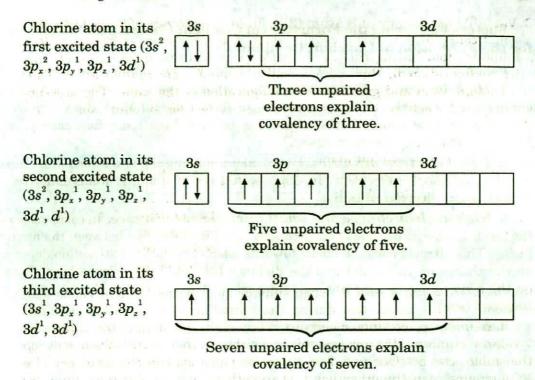


covalency of 6.

**3. Variable covalency of Cl atom (1, 3, 5, 7).** Covalencies of Cl atom equal to 1, 3, 5 and 7 can be explained as follows :



explains covalency of one.



It may be seen from the above discussion that variable covalency is shown only by those elements whose atoms have vacant d-orbitals in their valence shell so that the unpairing of s- and p-electrons by promoting them to vacant dorbitals may be possible. The elements having no d-orbitals (i.e. elements of 2nd period) do not exhibit variable covalency. Thus we can explain why molecules like NCl<sub>5</sub> and OF<sub>6</sub> do not exist.

#### **Maximum Covalency**

Maximum covalency of an element may be defined as the maximum number of covalent bonds formed by that element. For example the maximum covalency of P, S, and Cl atoms is 5, 6, and 7 respectively. It may be seen form the discussion on Variable Covalency that the maximum covalency exhibited by an element is equal to the number of unpaired electrons obtained after promoting all the s- and p-electrons to d-orbitals. This type of promotion makes all the electrons unpaired and the number of unpaired electrons obtained is equal to the maximum covalency of the atom under consideration.

## **Formation of Covalent Bonding and Periodic Table**

Covalent bonds are formed between the same or different kinds of atoms which should have high electronegativity, since the elements with high electronegativity do not ionise and have an equal attraction for electrons to complete their octets. Such elements are mostly located in right-hand portion of the periodic table.

## Factors Favouring the Formation of Covalent Compounds : Conditions for the Formation of Covalent Compounds

Following are the main factors which favour the formation of covalent bond.

1. *High ionisation Energy.* The atoms which have high value of ionisation energy are incapable of losing electrons to form cations. Thus these elements cannot form ionic bonds. Rather, they, due to their high ionisation energy, can form covalent bonds between them.

2. Equal electron affinities. For covalent bonding the two atoms must have equal attraction for electrons. In other words the combining atoms must have almost equal electron affinities.

**3.** *High nuclear charge and small internuclear distance.* In covalent bond the electron charge becomes highly concentrated in the region between the atomic nuclei. This attracts both the nuclei towards itself. This force of attraction depends on the charge on the nuclei and the distance between them. Hence high charge on the bonding nuclei and smaller internuclear distance favour the formation of covalent bond.

4. Number of valence electrons. Each of the two atoms should have 5, 6 or 7 valence electrons (H atom has only one electron) so that both the atoms achieve the stable octet by sharing 3, 2 or 1 electron pair. The non-metals of VA, VIA and VIIA groups respectively satisfy this condition.

5. Equal electronegativity. Both atoms should have equal electronegativity so that the transfer of electron (s) from one atom to the other may not take place, *i.e.*, ionic bond may not be formed. When the electronegativity of both the atoms is equal, sharing of electron pair(s) occurs and covalent bond is established.

## **Properties of Covalent Compounds**

1. Physical state. Covalent compounds usually consist of discrete molecules and the force of attraction between adjacent covalent molecules is weak. It is due to these weak forces that most of the covalent compounds exist as gases or liquids of low boiling points under the normal conditions of temperature and pressure. However, they may exist as soft solids only when their molecular weights are high; e.g. chlorine (mole. wt. = 71) is a gas, bromine (mol. wt. = 160) is a liquid, while iodine (mol. wt. = 254) is a solid.

2. Crystal structure. The crystals of covalent solids are of the two types :

(a) Those in which every atom is bonded with other atoms by covalent bonds resulting in the formation of giant molecules. Examples of giant molecules are diamond, silicon carbide (SiC), aluminium nitride (AIN) etc.

(b) Those which consist of separate layers. The covalent compounds containing separate layers are said to have layer lattice structure. Examples of covalent compounds having layer structure are graphite,  $CdI_2$ ,  $CdCl_2$ , BN etc.

**3.** Melting and boiling points. With the exception of covalent solids consisting of giant molecules (e.g. diamond, SiC, AIN etc), other covalent solids have relatively lower melting and boiling, points than the ionic solids, e.g. boiling

points of SiCl<sub>4</sub> (covalent compound) and NaCl (ionic compound) are  $58^{\circ}$ C and 1440°C respectively. Low boiling points are due to the fact that the attractive forces between covalent molecules are *weak van der Waal's forces*.

4. Electrical conductivity. Covalent solids consisting of giant molecules are bad conductors of electricity, since they do not contain charged particles (*i.e.* ions) or electrons to carry the current. However the covalent solids having the layer lattices (*e.g.* graphite) are good conductors of electricity, since in such solids electrons can pass from one layer to the other and thus current can be carried. Certain covalent substances like HCl ionise in solution and their solutions conduct electricity.

**5.** Solubility in polar and non-polar solvents. With the exception of covalent solids consisting of giant molecules, all other covalent solids are *insoluble in polar solvents* like  $H_2O$  but are *readily soluble in non-polar solvents* like  $C_6H_6$ ,  $CCl_4$  etc. Their solubility in non-polar solvents is due to the similarity in covalent nature of the molecules of the solute and solvent, *i.e.*, their solubility is based on the principle : "Like dissolves like". Covalent solids having the giant molecules are insoluble in all the solvents. This is because of the fact that these solids, due to their big size, are not able to interact with the solvent molecules. Some of the covalent compounds like alcohol, amines etc. are soluble in  $H_2O$  due to hydrogen bonding.

6. Neither hard nor brittle. While ionic compounds are hard and brittle, covalent compounds are neither hard nor brittle. Rather they are soft and waxy, since they usually consist of separate molecules. There are weak forces holding the molecules in the solid crystal lattice. A molecular layer in the crystal easily slips relative to other adjacent layers and there are no forces of repulsion between the layers like those in ionic compounds. Thus covalent crystals are easily broken and there is no sharp cleavage between the layers on application of external force.

7. Molecular reactions. Covalent compounds undergo molecular reactions in solutions, *i.e.*, in solution covalent compounds give reactions where the molecule as a whole undergoes a change. Since there are no strong electrical forces to speed up the reaction between molecules, these reactions are slow and hence need a control of temperature and pressure.

8. Isomerism. Since covalent bonds are *rigid* and *directional*, they can give rise to different arrangements of atoms in space. So, a single molecular formula of a covalent compound may represent a number of different compounds with different properties. This means that covalent compounds can show isomerism. This phenomenon of isomerism is shown mostly by organic compounds.

#### **Comparison of the Properties of Ionic and Covalent Compounds**

The comparison of the properties of ionic and covalent compounds is shown in Table 7.1.

Property	Ionic compounds (Electrovalent compounds)	Covalent compounds
(i) Physical state	These are crystalline solids at room temperature. They are never liquids or gases under the ordinary conditions of temperature and pressures.	Most of the covalent compounds exist as gases or liquids. However, the covalent com- pounds having high molecular weight can exist as solids.
(ii) Crystal structure	They consist of three dimensional solid aggregates (ionic solids).	The crystals of covalent compounds are of two types : (a) those consisting of giant molecules (e.g. diamond etc.) (b) those consisting of separate layers (e.g. graphite, $CdI_2$ etc.).
(iii) Hardness and brittleness	These are hard and brittle, since the cations and anions are held together very tightly by very strong electrostatic forces of attration.	Solid covalent compounds are soft and waxy, since they usually consist of separate molecules. They are much readily broken.
(iv) Nature of reactions	They undergo ionic reactions (in solution) which are fast and instantaneous.	They undergo molecular reactions (in solution) which are slow.
(v) Melting and boiling points	They have usually high melting and boiling points, since very high amount of energy (in the form of heat) is required to separate the cations and anions against the forces holding them together in the ionic solids.	With the exception of giant molecules, other covalent solids have low melting and boiling points. This is because of the reason that the attractive forces between covalent molecules are weak van der Waal's forces.
(vi) Solubility in polar and non- polar solvents	They are freely soluble in polar solvents and insoluble or slightly soluble in nonpolar solvents. Their solubility in polar solvents is because of the reason that the solvation energy of the solvent is greater than the lattice energy of the ionic solid.	They are insoluble in polar solvents and readily soluble in non-polar solvents. Their solubility in non-polar solvents is based on the principle : "Like dissolves like".
(vii) Electrical conductivity	These are bad conductors when they are in the solid state. However, they conduct electricity in fused state or in solution in which their ions are free to migrate.	Covalent solids consisting of giant molecules are poor conductors because they do not contain charged particles or electrons to carry the current.
viii) Nature of bonds	(a) Formed by the transfer of electrons from a metal to a non-metal.	(a) Formed by the sharing of electron pair(s) between non- metal atoms
	<ul> <li>(b) Consist of electrostatic force between cations and anions.</li> <li>(c) Non-rigid and non-directional.</li> <li>(d) Cannot cause isomerism</li> </ul>	<ul> <li>(b) Consist of shared pair(s) or electrons between atoms</li> <li>(c) Rigid and directional</li> <li>(d) Cause streoisomerism.</li> </ul>

# Table 7.1. Comparison of the properties of ionic and covalent compounds

## Failure of Octet Rule (Lewis Concept) in Covalent Compounds

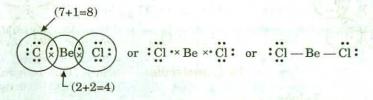
In the formation of a covalent bond, the atoms attain an inert gas configuration with an octet of electrons (*i.e.*,  $ns^2p^6$  configuration). This is known as **octet rule or rule of eight.** In H<sub>2</sub> molecule each of the two H.atoms. however, attains  $1s^2$  configuration (*doublet*).

## $H \cdot + H \rightarrow H : H \text{ or } H-H$

But there are many covalent molecules in which the central atom which is covalently bonded with other atoms has electrons either *less* than eight (*incomplete octet*) or *more* than eight (*expansion of octet*) in its outermost shell, *i.e.* in such molecules the central atom is surrounded by electrons either less or more than eight. In this way we come across many molecules which have *nonoctet structure*. Thus there are two types of deviations from the octet rule in covalent compounds.

1. Molecules in which the octet remains incomplete : Incomplete octet. Consider the structures of  $BeCl_2$ ,  $BF_3$ ,  $(CH_3)_3Ga$  and NO molecules as given below :

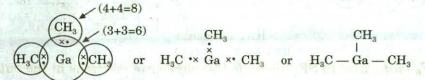
(a) **BeCl<sub>2</sub>** molecule. In this molecule Be atom (central atom) has only four electrons in its outermost shell-two of its own (shown by crosses) and the other two (shown by dots) from the two covalently bonded Cl atoms.



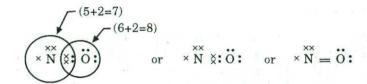
(b)  $BF_3$  molecule. In this molecule the boron atom (central atom) has only six electrons in its outermost shell-three of its own and the other three from the three covalently bonded F atoms.



(c) (CH<sub>3</sub>)<sub>3</sub>Ga molecule. Here Ga atom has six electrons in its outer-most shell.

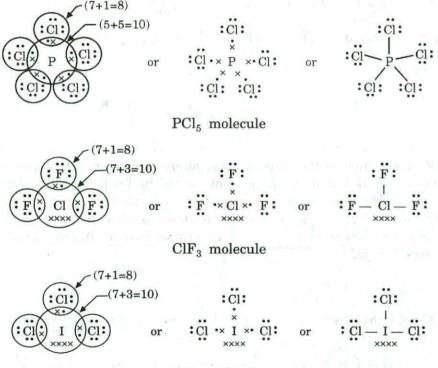


(d) NO molecule. Here N atom has only seven electrons (septet) in its outermost shell-five of its own and the other two from oxygen atom with which it is linked by a double bond. Note that oxygen atom has eight electrons in its outermost shell.



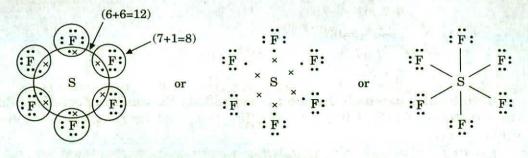
2. Molecules in which the octet is expanded : *Expansion of octet*. Consider the structures of  $PCl_5$ ,  $ClF_3$ ,  $ICl_3$ ,  $SF_6$ ,  $IF_7$ ,  $OsF_8$  and  $OsO_4$  molecules as given below :

(a)  $PCl_5$ ,  $ClF_3$  and  $ICl_3$  molecules. In  $PCl_5$  molecule the total number of electrons in the outermost shell of phosphorus atom (central atom) is *ten*-five electrons of its own  $(P \rightarrow 3s^2p^3)$  and five electrons gained by it in forming five covalent bonds with five chlorine atoms. Similarly in  $ClF_3$  and  $ICl_3$  molecules the number of electrons in the outermost shell of Cl and I atoms (central atoms) is also *ten*-seven electrons of their own  $(Cl \rightarrow 3s^2p^5, I \rightarrow 5s^2p^5)$  and three electrons gained by Cl and I atoms in forming three covalent bonds with three halogen atoms.



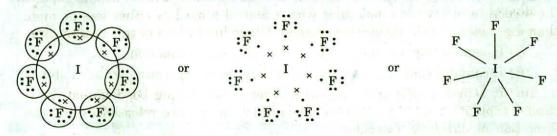
ICl<sub>3</sub> molecule

(b)  $SF_6$  molecule. In SF<sub>6</sub> molecule the number of electrons in the outermost shell of sulphur atom (central atom) is *twelve*—six electrons of its own (S  $\rightarrow$   $3s^2p^4$ ) and six electrons gained by S in forming six covalent bonds with six F atoms.



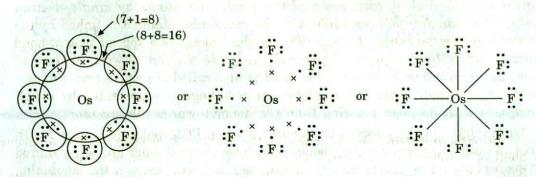
SF<sub>6</sub> molecule

(c)  $IF_7$  molecule. In  $IF_7$  molecule the number of electrons in the outermost shell of I atom (central atom) is *fourteen*—seven electrons of its own  $(I \rightarrow 5s^2p_5)$  and seven electrons gained by I atom in forming seven covalent bonds with seven F atoms.

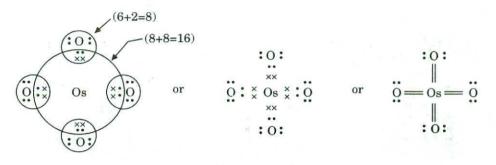


## IF<sub>7</sub> molecule

(d)  $OsF_8$  and  $OsO_4$  molecules. In  $OsF_8$  molecule the number of electrons in the outermost shell of Os atom (central atom) is sixteen—eight electrons of its own ( $Os \rightarrow 5d^6 6s^2$ ) and eight electrons gained by Os in forming eight covalent bonds with eight F atoms. Similary in  $OsO_4$  molecule the number of electrons in the outermost shell of Os atom (central atom) is sixteen—eight electrons of its own and eight electrons gained by Os in forming four double covalent bonds with four oxygen atoms.



## OsF<sub>8</sub> molecule



 $OsO_4$  molecule

Thus we see that in all the above molecules the octet of the central atom is expanded. The molecules containing central atoms with more than an octet of electrons are called **super octet structures**.

The above study makes it quite clear that Lewis concept is not able to explain the structure of covalent molecules whose central atom has either less or more than eight electrons in its outermost shell. Other limitations of this concept are :

(i) It cannot explain the cause of covalent bond formation.

(ii) It cannot explain the nature of attractive forces operating between atoms.

(*iii*) It cannot predict the amount of energy lost during bond formation. It cannot explain as to why different amounts of energy are released during the formation of different molecules.

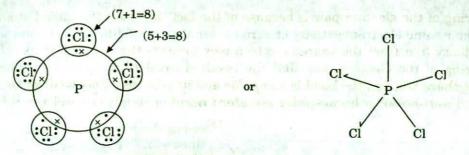
(iv) It cannot predict the geometry of a molecule (*i.e.* arrangement of atoms in space). For example, it can not explain as to why BF<sub>3</sub> is planar and NH<sub>3</sub> is pyramidal.

## **Explanation of the Failure of Octet Rule.**

The failure of octet rule in the formation of covalent molecules like those mentioned above has been explained with the help of the following concepts :

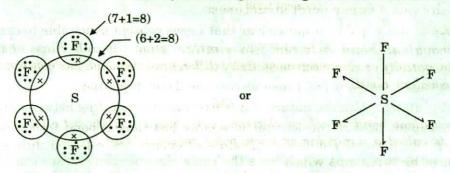
1. Sugden's concept of single linkages. Sugden postulated that the central atom of the molecules like  $PCl_5$ .  $SF_6$  etc. maintains its octet and in doing so the central atom is linked with some of the combining atoms by single-electron bonds, called singlet linkages while with the remaining atoms it is linked by the normal two-electron covalent bonds. The singlet linkage is a special type of bond which is formed by the one-sided sharing of only one electron between the central atom and the combining atoms. This bond is also called single-electron linkage, half-bond or simply singlet. A singlet-electron linkage is represented by a half arrow  $(\rightarrow)$  with its head pointing from the donor towards the acceptor.

On the basis of this concept phosphorus atom in  $PCl_5$  molecule is linked with three Cl atoms by three covalent bonds (*i.e.* three electron pairs are being shared between phosphorus and three chlorine atoms) and with each of the remaining two chlorine atoms it is linked by a singlet linkage. Thus the structure of  $PCl_5$ can be shown as follows :



Singlet linkage is weaker than a covalent bond and this explains why  $PCl_5$  readily dissociates into  $PCl_3$  and  $Cl_2$ .

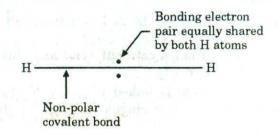
In  $SF_6$  molecule sulphur atom is linked with two F atoms by two covalent bonds and with four F atoms by four singlet linkages as shown below :



2. Sidgwick's concept of maximum covalency. According to this concept it is not necessary for an element to have a maximum covalency of four, *i.e.* it is not essential that an element be surrounded by  $4 \times 2 = 8$  electrons for its stability. The covalency of an element may exceed four and the octet can be expanded. The maximum covalency of an element actually depends on the period in which the element concerned is present. For hydrogen (first period with n = 1) it is 2, for the elements of 2nd period with n = 2 (Li to F) it is 4, for the elements of 3rd (n = 3) and 4th (n = 4) periods it is equal to 6 and for those in higher periods (n > 4) it is equal to 8. Consequently maximum capacity of the valence shell of an atom to have electrons (or maximum number of electrons being shared) for the elements mentioned above is equal to  $2 \times 2 = 4$ ,  $4 \times 2 = 8$ ,  $6 \times 2 = 12$  and  $8 \times 2 = 16$  respectively. Thus we see that there is no anomaly in compounds like PCl<sub>5</sub>, SF<sub>6</sub>, OsF<sub>8</sub> etc. having central atoms making five, six and eight covalent bonds with the combining atoms respectively.

## Covalent Bonds Having Partial Ionic Character : Non-polar and Polar Covalent Bonds

1. Covalent bond between two similar atoms-Non-polar covalent bond. The bonding electron pair constituting the covalent bond between two similar atoms which have the same electronegativity or zero electronegativity difference is equally shared by both the linked atoms, i.e. the shared electron pair is placed at the centre of the distance between the nuclei of the linked atoms. The equal sharing of the electron pair is because of the fact that both the linked atoms, due to their same electronegativity or zero electronegativity difference, have the same tendency to attract the shared electron pair towards them. It is because of equal sharing of the electron pair that the resulted covalent bond has no polarity or ionic character, *i.e.*, the bond is *non-polar* and *non-ionised*. This bond is, therefore, called **non-polar** or **homo-polar covalent bond** or simply **covalent bond**.



Thus :

A covalent bond between two similar atoms which have the same electronegativity or zero electronegativity difference is called a non-polar or homopolar covalent bond.

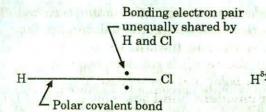
#### OR

A covalent bond in which electrons are shared equally between the linked atoms is called a non-polar or homo-polar covalent bond.

Since the two atoms which have the same electronegativity are the atoms of the same element, all covalent bonds between two similar atoms are non-polar or homo-polar covalent bonds.

A non-polar covalent bond is a true or purely covalent bond, since it has no or negligible polarity or ionic character. H–H, F–F etc are the examples of nonpolar covalent bonds. The molecules like  $H_2$ ,  $F_2$  etc which have non-polar covalent bonds are called **non-polar molecules**. Such molecules are the true covalent compounds.

**2.** Covalent bond between two dissimilar atoms-Polar covalent bond. The bonding electron pair constituting the covalent bond between two dissimilar atoms like H and Cl which have different electronegativity values (H = 2.1, Cl = 3.3) is not equally shared by the linked atoms, i.e. the electron pair is not placed at the centre of the distance between the nuclei of the two atoms viz. H and Cl. Rather, it is partially displaced (i.e. attracted) towards the more electronegative Cl atom owing to its greater affinity for electron pair. This type of partial displacement of the shared electron pair towards the more electronegative Cl atom develops a small (fractional) negative charge (represented as  $\delta$ -) on more electronegative Cl atom and an equal amount of small positive charge (represented as  $\delta$ +) on less electronegative H atom, and HCl molecule appears to be containing two oppositely charged poles (called charge-centres or electrical poles) namely H<sup>\delta+</sup> and Cl<sup> $\delta$ -</sup> at the end of the bond and the molecule is depicted as H<sup> $\delta$ +</sup>-Cl<sup> $\delta$ -</sup>. The covalent bond between H and Cl atoms develops some polarity or partial ionic character and hence is called *polar covalent bond*.



Thus polar covalent bond can be defined as follows :

A covalent bond between two dissimilar atoms which have different electronegativity values is called a polar covalent bond.

#### OR

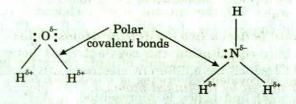
A covalent bond in which electrons are shared unequally between the linked atoms and the linked atoms acquire fractional positive and negative charge is called a polar covalent bond.

Polar covalent bond is not a true or purely covalent bond, since it has some polarity or ionic character. Thus it is neither wholly covalent nor wholly ionic but has an intermediate character. The molecules like HCl which have polar covalent bonds are called **polar molecules**.

Since the linked atoms having different electronegativity may not be the atoms of the same elements, all covalent bonds between two dissimilar atoms are polar covalent bonds. For example :

(a)  $H_2O$  molecule contains two O-H covalent bonds. Since H and O atoms have different electronegativity (H = 2.1, O = 3.5), both O-H covalent bonds are polar covalent bonds and  $H_2O$  is a polar molecule.

(b)  $NH_3$  molecule has three N-H covalent bonds. Since H and N have different electronegativity (H = 2.1, N = 3.0), all the three N-H covalent bonds are polar covalent bonds and  $NH_3$  is a polar molecule.



#### Percentage of Ionic Character in a Polar Covalent Bond

If two atoms A and B are linked together by a polar covalent bond  $(A^{\delta-} - B^{\delta+})$ , the amount of ionic character in this bond depends on the difference of electronegativity values of A and B. Greater is the difference,  $(x_A - x_B)$ , greater is the percentage of ionic character in A-B bond. Here the electronegativity of atom A  $(x_A)$  has been assumed to be higher than that of B  $(x_B)$ . This point can be illustrated by considering the nature of X-H bond in halogen acids of HX type (e.g. HF, HCl, HBr and HI). The polarity of H-X bond in HX acids increases with the increase of electronegativity difference,  $(x_X-x_H)$ . Since electronegativity of H atom (i.e.  $x_H$ ) remains the same throughout the series, the polarity of H-X bond increases with the increase of electronegativity of X atom (i.e.,  $x_X$ ). Thus the polarity (i.e., ionic character) in H-X bond is in the following order :

$$H-F > H-Cl > H-Br > H-I.$$

Consequently HF acid is the most polar while HI is the least so.

Pauling has estimated the approximate percentage of ionic character in various A-B polar covalent bonds from known  $(x_A-x_B)$  values and has prepared a table (given below) which gives a relation between  $(x_A-x_B)$  values, percentage ionic character in A-B bond and the nature of this bond.

Table. Relation between  $(x_A-x_B)$  values, percentage ionic character in A-B bond and the nature of A-B bond  $(x_A > x_B)$ .

$(x_{\rm A} - x_{\rm B})$	% ionic character in A-B bond	Nature of A-B bond and its representation	Examples of bonds
0		Purely covalent (A-B)	N=N, O=O, Cl-Cl, H-H.
0.1-0.8	0.5-15	Covalent (A-B)	C-S, C-I, N-Cl, P-H
0.9–1.6	19–47	Polar covalent $(A^{\delta_{-}} - B^{\delta_{+}})$	Both O-H bonds in H <sub>2</sub> O molecule are polar covalent bonds and are represented as O <sup>8-</sup> -H <sup>8+</sup>
1.9	50	50% ionic and 50% covalent	
1.9-2.0	55-63	Ionic (A <sup>-</sup> -B <sup>+</sup> )	
2.0-2.3	67-74	Ionic (A <sup>-</sup> -B <sup>+</sup> )	Na-Cl (Na+Cl-)
2.3-3.3	76-93	Ionic (A <sup>-</sup> -B <sup>+</sup> )	Cs-F (Cs+F-)

The following points may be noted from the above table :

(i) When  $(x_A - x_B) = 1.9$ , the amount of ionic character in A-B bond is 50% and that of covalent character is also 50%. Thus A-B bond is 50% ionic and 50% covalent.

(ii) When  $(x_A-x_B) < 1.9$ , the amount of ionic character in A-B bond is less than 50% and that of covalent character is more than 50%. Thus A-B bond is predominantly covalent and hence is represented as A-B.

(*iii*) When  $(x_A-x_B) > 1.9$ , the amount of ionic character in A-B bond is more than 50% and that of covalent ,character is *less* than 50%. Hence A-B bond is predominantly ionic and hence is represented as A<sup>-</sup> B<sup>+</sup>.

Hanny and Smyth Equation.

Hanny and Smyth took some heterodiatomic molecules of AB type like HF, HCl, HBr, HI, NaI, KI, KCl, etc and plotted a graph between the percentage of ionic character in A-B bond and electronegativity difference,  $(x_A-x_B)$ . With the help of this graph they obtained the following equation which gives the percentage of ionic character in a given A-B bond in AB molecule.

% ionic character in A-B bond	$= [0.16(x_{\rm A} - x_{\rm B}) + 0.035(x_{\rm A} - x_{\rm B})^2] \times 100\%$	70
and a providence of a state of the	$= [16(x_{\rm A}-x_{\rm B}) + 3.5(x_{\rm A}-x_{\rm B})^2]\% \qquad(i)$	)

430

#### Solved Examples

**Example 1.** Calculate the percentage of ionic character in Cs-F bond in CsF molecule. The electronegativity values of Cs and F are 0.7 and 4.0 respectively. Predict the nature of CsF molecule.

**Solution.**  $x_{\rm A} - x_{\rm B} = x_{\rm F} - x_{\rm Cs} = 4.0 - 0.7 = 3.3$ 

:. % ionic character in Cs-F bond =  $[16 \times 33 + 3.5 \times (3.3)^2]\%$ 

= 90.9%

Since the ionic character is more than 50%, CsF is a purely ionic molecule.

**Problem 2.** Calculate the percentage of ionic character in K-Cl bond in KCl molecule. The electronegativity values of K and Cl are 0.8 and 3.0 respectively. Also predict the nature of KCl molecule.

**Solution.**  $x_{A}-x_{B} = x_{CI}-x_{K} = 3.0 - 0.8 = 2.2$ 

:. % ionic character in K-Cl bond =  $[16 \times 2.2 + 3.5 \times (2.2)^2]$ %

= 52.1%

Since the ionic character is more than 50%, KCl is an ionic molecule.

**Problem 3.** Calculate the percentage of ionic character in Na–Cl bond in NaCl molecule. Also predict the nature of NaCl molecule ( $x_{Na} = 0.9$  and  $x_{Cl} = 3.0$ ).

Solution.  $x_{A} - x_{B} = x_{CI} - x_{Na} = 3.0 - 0.9 = 2.1$ 

% ionic character in Na–Cl bond =  $[16 \times 2.1 + 3.5 \times (2.1)^2]$ %

= 49%

Since the ionic character is less than 50%, NaCl is a covalent molecule. (According to Hanny and Smyth's equation)

**Example 4.** Arrange the molecules HF, HCl, HBr and HI in the decreasing order of the percentage of ionic character in H-X bond (X = F, Cl, Br or I). Electronegativity values are as : F = 4.0, Cl = 3.0, Br = 2.8, I = 2.2, and H = 2.1.

**Solution.** If we substitute the electronegativity values of F, Cl, Br I and H atoms in Hanny and Smyth's equation [equation (i)], the percentage of ionic character in H-X bonds in HF, HCl, HBr and HI molecules is found as given below :

%	ionic	: (	chara	cter	in	H-F	bond	and	HF	m	olecu	le	=	43%
"	37	"	"	"		H-Cl	"		"	"	HCl	"	=	17%
"	"	"	"	"		H-Br	. "	"	"	"	HBr	"	=	13%
"	"	"	"	"		H–I	"	"	"	"	HI	22	=	7%

Thus we see that the percentage of ionic character in H-X bonds in the above molecules is in the following decreasing order :

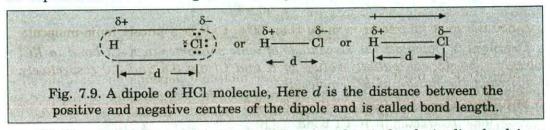
H-F > H-Cl > H-Br > H-I

#### Properties of Polar Molecules

Polar molecules have the following properties :

(i) The properties of polar compounds are intermediate between those of purely covalent and purely ionic compounds.

(*ii*) A polar molecule like HCl  $(H^{\delta+} - Cl^{\delta-})$  which has positive and negative charge centres or electrical poles, as they are called, at the ends of the covalent bond, becomes dipolar and hence is called a **dipole** (two poles). Sidgwick (1930) proposed that a dipole of a bond may be shown by an arrow with a crossed tail. The arrow is placed parallel to the line joining the points of charge and should be from positive to negative end of the dipole. Thus a dipole of HCl molecule may be depicted as shown in Fig. 7.9. The dipole behaves as a small magent.



(iii) Dissolution in polar solvents. When a polar molecule is dissolved in a colar solvent like  $H_2O$ , the polar molecules of water surround the positive and negative ends of the polar covalent compound (solute) and split it into cations and anions which are surrounded by a definite, but unknown, number of water molecules. For example when HCl molecule, which is a polar covalent molecule, is dissolved in water, the polar molecules of  $H_2O$  break HCl ( $H^{\delta+} - Cl^{\delta-}$ ) molecule into  $H^{\delta+}$  and  $Cl^{\delta-}$  ions which are surrounded by water dipoles as shown in Fig. 7.10.

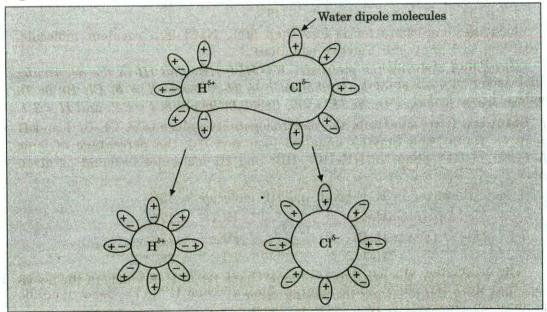


Fig. 7.10. Dissolution and ionisation of HCl in water.

(iv) Dipole moment. The degree of polarity of a polar covalent bond or of a polar molecule (*i.e.* a molecule having a polar covalent bond) is expressed in terms of its *dipole moment* ( $\mu$ ) which is equal to the product of the magnitude of electric charge (e) in esu and distance (d) in A° between the positive and negative centres (*i.e.* bond length).

Thus :

$$u = e \times d$$

As e is of the order of  $10^{-10}$  esu and d of the order of  $10^{-8}$  cm,  $\mu$  is of the order of  $10^{-10} \times 10^{-8}$  esu. cm or  $10^{-18}$  esu. cm and this unit of  $\mu$  is known as Debye (D). Thus :

$$1 D = 10^{-18} esu. cm$$
  
= 10<sup>-10</sup> esu. A°  
= 3.33 × 10<sup>-28</sup> coulomb. cm

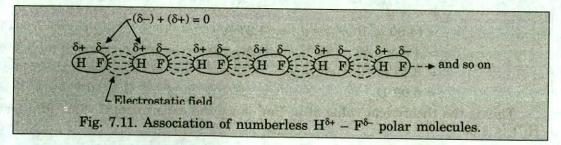
µ is a vector quantity.

Magnitude of dipole moment of a polar molecule depends on the difference in electronegativities of the bonded atoms. The greater the difference in electronegativities, the greater is the dipole moment. Consequently greater is the value of dipole moment of a polar molecule, greater is the degree of polarity of the polar covalent bond between the linked atoms (See Table 7.1).

Table 7.1. Relation between the dipole moment value and the degree of polarity (i.e. percent of ionic character) of H-X covalent bond.

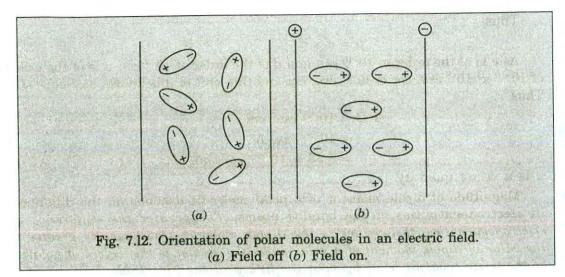
Molecule	Dipole moment value (in D)	% ionic character of H-X bond (X = I, Br, Cl, F)
H—I	0.38	5
H—Br	0.87	12
H—Cl	1.03	17
H—F	1.92	1000 The second 3 10 Paral second

(v) Polar molecules have great attraction for each other and arrange themselves into an endless chain and thus get associated with each other as shown below in Fig. 7.11 for  $H^{\delta_+} - F^{\delta_-}$  polar molecules.



The association of polar molecules to form an endless chain is because of the fact that the alternate  $\delta^+$  and  $\delta^-$  charges on individual  $H^{\delta_+} - F^{\delta_-}$  polar molecules produce an electrostatic field between them.

(vi) Orientation in electric field. Due to dipole moment, polar molecules tend to be oriented in an electric field. The positive ends of dipoles are directed towards the negative electric plate while the negative ends towards the positive plate (Fig. 7.12). Measurements based on the orientation of polar molecules in electric field have been used to calculate the dipole moments.



# Applications of Dipole Moment

1. Amount of ionic character in a bond. The value of dipole moment can be used for determining the amount of ionic character in a bond. The dipole moments of diatomic non-polar molecules like  $H_2$ ,  $Cl_2$ ,  $F_2$  etc are zero. Greater is the degree of polarity of a diatomic molecule, the larger will be its dipole moment.

Let us find out the percent of ionic character of H–Cl bond in HCl molecule with the help of dipole moment value of this molecule. Suppose that HCl molecule is *completely* ionic. Under this condition H<sup>+</sup> and Cl<sup>-</sup> ions would bear a unit charge equal to  $4.80 \times 10^{-10} \ e.s.u.$  (= e) and the bond distance between H and Cl atoms =  $1.27 \ A^{\circ}$  (= d).

Thus :

$$\begin{split} \mu &= e \times d \\ &= (4.80 \times 10^{-10} \ e.s.u.) \times (1.27 \ \text{A}^{\circ}) \\ &= 4.8 \times 1.27 \times 10^{-10} \ e.s.u. \ \text{A}^{\circ} \\ &= 6.19 \times 10^{-10} \ e.s.u. \ \text{A}^{\circ} \\ &= 6.09 \ \text{D} \end{split}$$

 $(:: 1 D = 10^{-10} e.s.u. A^{\circ})$ 

This is the theoretical value of  $\mu$ . But, since the experimental value of  $\mu$  for HCl is 1.03,

 $\begin{array}{l} \label{eq:constraint} \% \ ionic \ character \ in \ H-Cl \\ bond \ in \ HCl \ molecule \end{array} \right\} \ = \frac{Experimental \ value \ of \ \mu}{Theoretical \ value \ of \ \mu} \times 100\%$ 

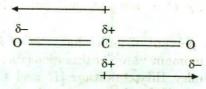
$$=\frac{1.03}{6.09} \times 100\% = 0.169 \times 100\%$$
$$= 16.9\% \approx 17\%$$

This means that H-Cl bond in HCl molecule has 17% ionic character and hence 83% covalent character.

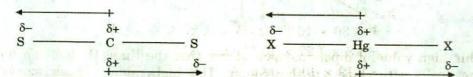
2. Geometry and shape of molecules. Dipole moment value of a molecule also helps in determining its geometry and shape.

The diatomic molecules composed of similar atoms (e.g.  $H_2$ ,  $Cl_2$  etc.) have no dipole moment, but those having different atoms (e.g. HF, HCl, HBr, HI etc.) do have some value of dipole moment. Symmetrical linear polyatomic molecules like  $CCl_4$ ,  $CO_2$ ,  $CS_2$ ,  $HgX_2$  (X = Cl, Br, I) etc. have zero resultant dipole moment and hence are non-planar, since dipole moments for all the bonds present in the molecule cancel each other in opposite directions. On the other hand unsymmetrical non-linear polyatomic molecules like  $H_2O$ ,  $H_2S$ ,  $SO_2$ ,  $NO_2$  etc. have some value of dipole moment and hence are polar molecules. Thus the value of the dipole moment of a molecule gives an information about its geometry. Following examples will illustrate this point.

(a)  $CO_2$ ,  $CS_2$ , and  $HgX_2$  molecules. These are triatomic symmetrical molecules.  $CO_2$  molecule (O=C=O) is non-polar, although C=O bonds are polar as the shared electron pair lies closer to O-atom than to C-atom on account of higher electronegativity of O-atom. This molecule has zero dipole moment. Zero dipole moment value and non-polar nature of the molecule can be explained only when it is assumed that the molecule is *linear* so that the dipole moment of one  $C^{\delta_+} - O^{\delta_-}$  bond on one side cancels that of the same bond on the other side.

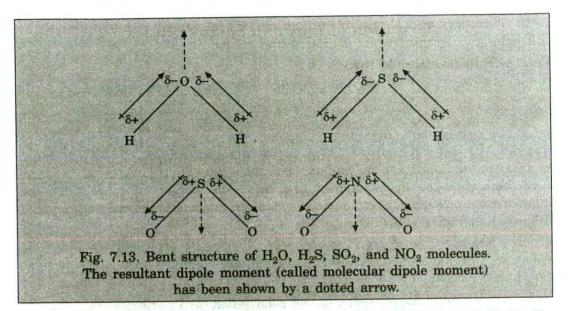


Similar arguments can be made to explain that  $CS_2$  and  $HgX_2$  molecules are non-polar, have zero dipole moment and hence are linear.

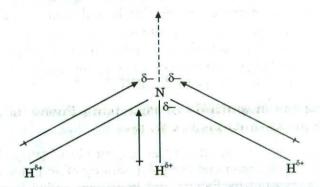


(b)  $H_2O$ ,  $H_2S$ ,  $SO_2$  and  $NO_2$  molecules. Although these are also triatomic molecules like  $CO_2$ ,  $CS_2$  and  $HgX_2$  molecules, yet these have some value of dipole moment (e.g.  $H_2O = 1.85$  D,  $SO_2 = 1.60$  D, etc). This clearly shows that there is no possibility for these molecules to have a linear shape as  $CO_2$ ,  $CS_2$  and  $HgX_2$ have. Rather these molecules have bent structure (Fig. 7.13) to give rise to the resultant dipole moment. In these molecules there are two dipolar bonds and the resultant of the dipole moment of these individual dipolar bonds gives the dipole moment of the molecule, called molecular dipole moment. The molecular dipole moment of these molecules has been shown by a dotted arrow.

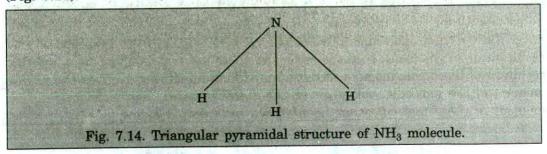
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(c)  $NH_3$  molecule. It is a tetratomic molecule and contains three dipolar  $N^{\delta-}-H^{\delta+}$  bonds and their resultant gives the molecular dipole moment which has been found experimentally equal to 1.46 D.



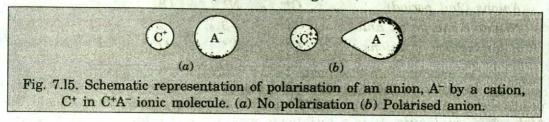
This high value of dipole moment shows that the three H-atoms do not lie symmetrically with respect to the N-atom. This high value of dipole moment is explained by giving a *triangular pyramidal structure* to this molecule, in which N-atom is situated at the apex and three H-atoms lie at the other three corners (Fig. 7.14).



## **Polarisation of Ions and Fajans's Rules**

#### What is Polarisation of Ions?

When a cation,  $C^+$  of an ionic molecule,  $C^+A^-$  approaches closely the anion,  $A^-$ , it withdraws the electrons (*i.e.* electron cloud) of the anion towards itself and the symmetrical shape of the electron cloud of the anion gets distorted. Thus the electron cloud of the anion no larger remains symmetrical but is elongated towards the cation. In other words we say that the  $A^-$  anion is *distorted* (or *deformed* or *polarised*) by  $C^+$  cation and this phenomenon is called **distortion** (or **deformation** or **polarisation**) of  $A^-$  anion by  $C^+$  cation (Fig. 7.15).



The cation,  $C^+$  is also deformed by the anion,  $A^-$ , but due to smaller size of the cation, its electrons are strongly held to the nucleus and hence the cation is not polarised to an appreciable extent by a nearby anion, *i.e.*, the polarisation of a cation by an anion is regarded as negligible and hence we generally do not consider the polarisation of a cation by anion.

The ability of a cation to polarise a nearby anion is called its **polarising power** or **polarising ability** and the tendency of an anion to get distorted or polarised by a cation is called its **polarisability**.

# Factors Affecting the Magnitude of Polarising Power of a Cation and Polarisability of an Anion-Fajans's Rules

Following are the factors on which the magnitude of polarising power of a cation to polarise a nearby anion and the polarisability of an anion depends. These factors have been suggested by Fajans and hence are called **Fajans's Rules**.

1. Charge on cation or anion. The cation with higher positive charge attracts the electron cloud of the anion more strongly towards itself than the cation with smaller positive charge and hence polarises the anion more strongly. Consequently higher is the positive charge on the cation, greater is its polarising power to polarise a given nearby anion. For example in LiCl, BeCl<sub>2</sub>, BCl<sub>3</sub> and CCl<sub>4</sub> molecules, the polarising power of Li<sup>+</sup>, Be<sup>2+</sup>, B<sup>3+</sup> and C<sup>4+</sup> cations (cations of the same period) to polarise Cl<sup>-</sup> anion increases with the increase of positive charge on them as shown below :

Molecules	:	LiCl	14	BeCl,	Mar.	BCl,		CCL	
Cations (2nd period)	.:	Li+		Be2+	11.4	B <sup>3+</sup>		C <sup>4+</sup>	
Positive charge on cations	:	+1	<	+2	<	+3	<	+4	dier T
Polarising power of cations		Li <sup>+</sup>	<	Be <sup>2+</sup>	<	B <sup>3+</sup>	<	C <sup>4+</sup>	n la la

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An anion with higher negative charge repells the electron cloud of its outermost shell towards the cation more effectively and hence is polarised by the cation more strongly. Consequently higher is the negative charge on the anion, more strongly it will be polarised by a given cation i.e. more will be its polariability. For example in CH<sub>4</sub>, NH<sub>3</sub>, H<sub>2</sub>O and HF molecules, the polarisability of C<sup>4-</sup>, N<sup>3-</sup>, O<sup>2-</sup> and F<sup>-</sup> anions (anions of the same period) to be polarised by H<sup>+</sup> cation decreases from C<sup>4-</sup> to F<sup>-</sup>, since the magnitude of negative charge on these anions also decreases in the same direction as shown below :

Molecules	:	$CH_4$	$NH_3$	$H_2O$	HF
Anions (2nd period)	:	C <sup>4-</sup>	$N^{3-}$	$O^{2-}$	$F^{-}$
Negative charge on anions	:	-4 >	-3	> -2 >	-1
Polarisability of anions		C4->	$N^{3-}$	$> O^2 >$	$F^{-}$
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Thus in order to make a cation to polarise an anion *effectively*, both the positive charge on the cation and the negative charge on the anion should be *high*.

2. Size of the cation. The nucleus of a smaller cation is shielded to a lesser extent by the electron shells and, therefore, such a cation attracts the electron cloud of the anion more strongly than a larger cation. This means that smaller is the size of the cation, higher is its polarising power to polarise a given nearby anion. For example in BeCl<sub>2</sub>, MgCl<sub>2</sub>, CaCl<sub>2</sub>, SrCl<sub>2</sub> and BaCl<sub>2</sub> molecules the polarising power of Be<sup>2+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Sr<sup>2+</sup> and Ba<sup>2+</sup> cations (cations of the same group) to polarise Cl<sup>-</sup> ion decreases with the increase of their size as shown below :

Molecules		BeCl <sub>2</sub>	MgCl <sub>2</sub>	CaCl <sub>2</sub>	$SrCl_2$	$BaCl_2$
Cations (Group IIA)	:0	Be2+	$Mg^{2+}$	$Ca^{2+}$	$Sr^{2+}$	$Ba^{2+}$
		0.31	< 0.65	< 0.99	< 1.13 <	1.35
Polarising power of cations	:	Be <sup>2+</sup>	$> Mg^{2+}$	$> Ca^{2+}$	$> Sr^{2+} >$	$Ba^{2+}$
and a sure of a part of a		6 Julio	2	Decreasi	ing —	$\rightarrow$

**3. Size of the anion.** The electrons of the outer-most shell of a larger anion are less firmly bound to its nucleus and hence can be withdrawn by the cation more easily. Consequently a larger anion will be polarised by the cation more easily than a smaller anion. This means that larger is the size of the anion, more strongly or easily it will be polarised by a given cation, i.e. more will be its polarisability. For example in halides of a given cation (e.g. MX halides) the polarisability of halide ions (anions of the same group) will increase from  $F^-$  to  $I^-$ , since the size of these ions also increases in the same direction.

Halides	1	MF	MCl	MBr	MI
Halide ions (Group VII A)	1	F	$Cl^-$	Br <sup>-</sup>	<i>I</i> -
		1.36	< 1.81	< 1.95 <	2.16
Polarisability of halide ions	- 7	F	< <i>Cl</i> -	< Br <sup>-</sup> <	I-
1 Parts		-	Incre	pasing	>

4. Electronic configuration of the cation. Consider two different cations like  $Cu^+$  and  $Na^+$  which have nearly the same size ( $Cu^+ = 0.96$  Å and  $Na^+ = 0.95$  Å) and same charge (= +1) but have different valence-shell electronic configurations— $Cu^+$  has 18-electron valence-shell configuration ( $Cu^+ \rightarrow 3s^2p^6d^{10}$ ) while  $Na^+$  has 8-electron valence-shell configuration ( $Na^+ \rightarrow 2s^2p^6$ ). Out of these cations,  $Cu^+$  cation polarises the anions more strongly than  $Na^+$  cation. (The anion to be polarised must be the same). This means that a cation with 18electron valence shell configuration ( $ns^2p^6d^{10}$  configuration) has greater polarising power than that with 8-electron valence-shell configuration ( $ns^2p^6$  configuration). Greater polarising power of the cation with  $ns^2p^6d^{10}$  valence-shell configuration is because of the fact that the d-electrons of the 18-electron shell shield the nuclear charge of the cation less effectively than the s- and p-electrons of 8-electron shell. Hence the cation with 18-electron valence shell configuration behaves, as if it has greater nuclear charge on it. Greater nuclear charge increases the polarising power of the cation having 18-electron valence-shell configuration.

On similar grounds it can be explained that  $Ag^+$  cation  $(4s^2p^6d^{10})$  has greater polarising power than K<sup>+</sup> cation  $(3s^2p^6)$ .

# Variation of Polarising Power of Cations in a Period and a Group of the Periodic Table (*Periodic Tends of Polarising Power of Cations*)

(a) In a period. In moving from left to right in a period, the size of the cations decreases and the positive charge increases. Both these factors increase the polarising power of the cations from left to right in a period. For example the polarising power of the cations of 2nd period viz. Li<sup>+</sup>, Be<sup>2+</sup>, B<sup>3+</sup> and C<sup>4+</sup> to polarise Cl<sup>-</sup> anion in LiCl, BeCl<sub>2</sub>, BCl<sub>3</sub> and CCl<sub>4</sub> molecules increases from Li<sup>+</sup> to C<sup>4+</sup> with the decrease of their size and increase in their positive charge from +1 to + 4 as shown below :

Molecules :	LiCl	BeCl <sub>2</sub>	BCl <sub>2</sub>	CCla
Cations (2nd period) :	Li <sup>+</sup>	$Be^{2+}$	$B^{3+}$	C4+
Size of cations (Å) :	0.60	> 0.31	> 0.20 >	0.15
Positive charges :	+ 1		< + 3 <	+ 4
Polarising power of cations :	Li <sup>+</sup>	< Be <sup>2+</sup>	< B <sup>3+</sup> <	C <sup>4+</sup>
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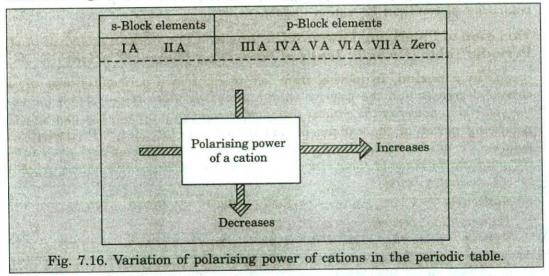
Similarly the polarising power of Na<sup>+</sup>, Mg<sup>2+</sup> and Al<sup>3+</sup> cations (cations of 3rd period) to polarise Cl<sup>-</sup> anion in NaCl, MgCl<sub>2</sub> and AlCl<sub>3</sub> molecules increases from Na<sup>+</sup> to Al<sup>3+</sup> with the decrease of their size and increase in their positive charge from + 1 to +3 as shown below :

Molecules	14121	NaCl	MgCl <sub>2</sub>	AlCl <sub>3</sub>
Cations (3rd period)	:	Na <sup>+</sup>	$Mg^{2+}$	Al <sup>3+</sup>
Size of cations (Å)	:	0.95 >	0.65 >	0.50
Positive charges	:	+ 1 <	+ 2 <	+ 3
Polarising power of cations	:	<i>Na</i> <sup>+</sup> <	$Mg^{2+} <$	Al <sup>3+</sup>
		Increa	sing —	$\rightarrow$

(b) In a group. On descending a group the magnitude of positive charge on the cations remains the same and hence it is the size of the cation alone which affects the magnitude of the polarising power of the given cation. On moving down a group the size of the cations increases and hence the polarising power of the cations goes on decreasing. For example the polarising power of the cations of the elements of Group IIA viz. Be<sup>2+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Sr<sup>2+</sup> and Ba<sup>2+</sup> to polarise Cl<sup>-</sup> ion in BeCl<sub>2</sub>, MgCl<sub>2</sub>, CaCl<sub>2</sub>, SrCl<sub>2</sub> and BaCl<sub>2</sub> molecules decreases with the increase of their size as shown below :

Molecules	:	$BeCl_2$	$MgCl_2$	$CaCl_2$	$SrCl_2$	$BaCl_2$
Cations (Group IIA)	:	$Be^{2+}$	$Mg^{2+}$	$Ca^{2+}$	$Sr^{2+}$	$Ba^{2+}$
Size of the cations (Å)	:	0.31	< 0.65 <	0.99 <	1.13 <	1.35
Polarising power of cations	:	$Be^{2+}$	$> Mg^{2+} >$	$Ca^{2+} >$	$Sr^{2+} >$	$Ba^{2+}$
				Decreasi	ng ——	$\longrightarrow$

The variation of polarising power of cations in the periodic table has been shown in Fig. 7.16.



## Variation of Polariability of Anions in a Period and a Group of the Periodic Table. (*Periodic Trends of Polarisability of Anions*)

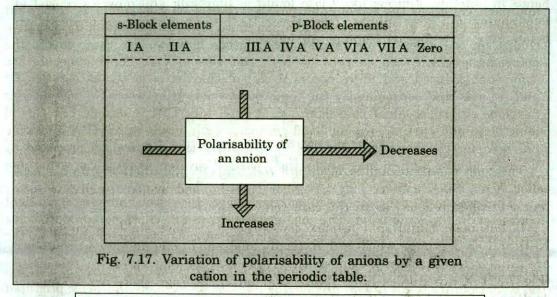
(a) In a period. We know that on proceeding from left to right in a period, both negative charge on the anions and their size decrease. Both these factors decreases the polarisability of the anions by a given cation from left to right in a period of the long form of periodic table. For example the polarisability of C<sup>4-</sup>, N<sup>3-</sup>, O<sup>2-</sup> and F<sup>-</sup> anions (anions of 2nd period) to be polarised by M<sup>+</sup> cations in M<sub>4</sub>C, M<sub>3</sub>N, M<sub>2</sub>O and MF molecules decreases from C<sup>4-</sup> to F<sup>-</sup>, since both negative charge on these anions and their size decrease in the same direction as shown below :

Molecules		M <sub>4</sub> C	M <sub>3</sub> N	M <sub>2</sub> O	MF
Anions (2nd period)	•	C4-	N <sup>3-</sup>	0 <sup>2</sup> -	F <sup></sup>
Negative charge on anions	:	- 4	> - 3	> - 2	> - 1
Size of anions (Å)	:	2.60	> 1.71	> 1.40	> 1.36
Polarisability of anions	:	$C^{4-}$	$< N^{3-}$	< 02-	< F-
Carl and the		-	- Decre	easing —	

(b) In a group. On descending a group, the magnitude of negative charge on the anions remains the same and hence it is the size of the anion alone which affects the magnitude of polarisability of a given anion. On moving down a group the size of the anions increases and hence the polarisability of the anions also goes on increasing. For example in the halides of a given cation (e.g. MX type halides) the polarisability of halide ions (anions of the same group) will increase from  $\mathbf{F}$  to I<sup>-</sup>, since the size of these anions also increases in the same direction as shown below :

Halides	:	MF	MCl	MBr	MI
Halide ions (Group VII A)	:	<b>F</b> ⁻	Cl-	Br-	<i>I</i> -
Size of halide ions (Å)	:	1.36 <	1.81 <	1.95 <	2.16
Charge on halide ions	:	- 1	- 1	- 1	- 1
Polarisability of halide ions		$F^{-} <$	<i>Cl</i> <sup>-</sup> <	$Br^- <$	<i>I</i> -
		and the second	- Incre	asing	$\rightarrow$

The variation of polarisability of anions by a given cation in the periodic table has been shown in Fig. 7.17.

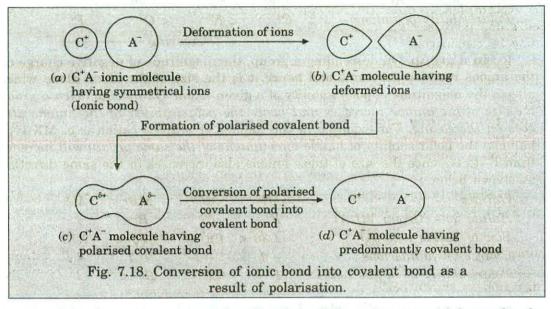


### **Applications of Polarisation of Ions : Fajans's Rules**

A. Degree of covalent character in ionic bond : Tendency of ions to form covalent bond : Fajans's rules. When the ions  $C^+$  and  $A^-$  of an ionic molecule,  $C^+A^-$  whose both the ions are symmetrical [Fig. 7.18 (a)] come closer to each other, each of the ions gets distorted or polarised by the other ion. But the

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polarisation produced by C<sup>+</sup> cation in A<sup>-</sup>anion is *appreciable* while that produced by A<sup>-</sup> in C<sup>+</sup> cation is negligible, *i.e.* C<sup>+</sup> cation is distorted by A<sup>-</sup> anion to a smaller extent while A<sup>-</sup> anion is distorted by C<sup>+</sup> cation to a larger extent, Now C<sup>+</sup>A<sup>-</sup> molecule has distorted ions [Fig. 7.18 (b)].



In the polarisation process the electrons of the anion are withdrawn by the cation towards itself. As the electrons withdrawn by the cation from the anion approach closer to the cation, the positive charge on the cation is somewhat reduced. Similary, as the electrons of anion move towards the cation, the negative charge on the anion is also somewhat reduced. Thus we see that, due to the polarisation effect, the charges on both the ions of C<sup>+</sup>A<sup>-</sup> ionic molecule are somewhat reduced and there occurs a sort of sharing of electrons between C<sup>+</sup> and A<sup>-</sup> ions and consequently the ionic bond existing between C<sup>+</sup> and A<sup>-</sup> ions develops partial covalent character, *i.e.* at this stage C<sup>+</sup>A<sup>-</sup> molecule has partial ionic bond and partial covalent bond character or in other words C<sup>+</sup>A<sup>-</sup> molecule has polarisd covalent bond [Fig. 7.18 (c)]. Now, if the polarisation produced by C<sup>+</sup> in A<sup>-</sup> is very high in magnitude, the polarised covalent bond is converted into predominantly covalent bond [Fig. 7.18 (d).

Thus we see that the process of polarisation produces some amount of covalent character in the ionic bond. The magnitude of covalent character produced due to polarisation effect depends on the amount of polarisation produced in the anion by the cation (or on the magnitude of polarising power of the cation) or polarisability of the anion. Greater the magnitude of polarising power of a cation or polarisability of an anion, greater the amount of covalent character produced in the ionic bond. Consequently the conditions which bring about the maximum polarisation of anions by given cations are, in fact, the conditions to make the bond covalent. These conditions are called **Fajans's rules** and are given below :

1. Charge either on cation or on anion should be large. Higher the positive charge on the cation, greater its polarising power to polarise a nearby anion. The

increase in polarising power of the cation increases the covalent character of the bond. Similarly higher the negative charge on the anion, higher will be its polarisability. The increase in polarisability is accompanied by an increase in the covalent character of the bond.

**Examples.** In order to understand how the large charge either on cation or on anion increases the covalent character of the bond, the following examples may be considered.

(a) The covalent character of Li<sup>+</sup>-Cl<sup>-</sup>, Be<sup>2+</sup>-Cl<sup>-</sup>, B<sup>3+</sup>-Cl<sup>-</sup> and C<sup>4+</sup>-Cl<sup>-</sup> bonds in LiCl, BeCl<sub>2</sub>, BCl<sub>3</sub> and CCl<sub>4</sub> molecules increases in the following order :

$$Li^{+}-Cl^{-} < Be^{2+}-Cl^{-} < B^{3+}-Cl < C^{4+}-Cl^{-}$$

since the polarising power (or positive charge) of  $Li^+$ ,  $Be^{2+}$ ,  $B^{3+}$  and  $C^{4+}$  cations (cations of the same period) to polarise  $Cl^-$  anion also increases in the same direction as shown below : (charges are given in parentheses)

$$Li^{+}(+1) < Be^{+2}(+2) < B^{+3}(+3) < C^{+4}(+4)$$

(b) Similarly the covalent character of Na<sup>+</sup>-Cl<sup>-</sup>, Mg<sup>+2</sup>-Cl<sup>-</sup> and Al<sup>+3</sup>-Cl<sup>-</sup> bonds in NaCl, MgCl<sub>2</sub> and AlCl<sub>3</sub> molecules increases in the following order :

$$Na^{+}-Cl^{-} < Mg^{+2}-Cl^{-} < Al^{+3}-Cl$$

since the polarising power (or positive charge) of Na<sup>+</sup>, Mg<sup>+2</sup> and Al<sup>+3</sup> cations (cations of the same period) to polarise  $Cl^-$  anion also increases in the same direction as shown below :

$$Na^{+}(+1) < Mg^{+2}(+2) < Al^{+3}(+3)$$

(c) The covalent character (i) of  $\text{Ge}^{2+}-X^-$  and  $\text{Ge}^{4+}-X^-$  bonds in  $\text{GeX}_2$  and  $\text{GeX}_4$  molecules (ii) of  $\text{Sn}^{2+}-X^-$  and  $\text{Sn}^{4+}-X^-$  bonds in  $\text{SnX}_2$  and  $\text{SnX}_4$  molecules, and (iii) of  $\text{Pb}^{2+}-X^-$  and  $\text{Pb}^{4+}-X^-$  bonds in  $\text{PbX}_2$  and  $\text{PbX}_4$  molecules increases in the order :

$$Ge^{2+}-X^- < Ge^{4+}-X^-$$
  
 $Sn^{2+}-X^- < Sn^{4+}-X^-$   
 $Pb^{2+}-X^- < Pb^{4+}-X^-$ .

since the polarising power (or the positive charge) of different cations (same group) to polarise  $X^-$  anion also increases in the same direction as shown below (positive charges carried by the cations are given in parentheses) :

$$Ge^{2+}(+2) < Ge^{4+}(+4)$$
  
 $Sn^{2+}(+2) < Sn^{4+}(+4)$   
 $Pb^{2+}(+2) < Pb^{4+}(+4)$ 

Thus the halides of  $Ge^{2+}$ ,  $Sn^{2+}$  and  $Pb^{2+}$  are largely ionic while those of  $Ge^{4+}$ ,  $Sn^{4+}$  and  $Pb^{4+}$  are largely covalent. Note that all the cations are of the same group (Group IVA).

In general we can say that if a metal forms halides in different oxidation states, the halides having the metal ion in lower oxidation state are largely ionic while those having the metal in higher oxidation state are largely covalent.

(d) The covalent character of H<sup>+</sup>-C<sup>4-</sup>, H<sup>+</sup>-N<sup>3-</sup>, H<sup>+</sup>-O<sup>2-</sup> and H<sup>+</sup>-F<sup>-</sup> bonds in CH<sub>4</sub>, NH<sub>3</sub>, H<sub>2</sub>O and HF molecules decreases in the order :

$$H^+-C^{4-} > H^+-N^{3-} > H^+-O^{2-} > H^+-F^-,$$

since the polarisability (or negative charge) of C<sup>4-</sup>, N<sup>3-</sup>, O<sup>2-</sup> and F<sup>-</sup> anions (same period) to be polarised by H<sup>+</sup> cation also decreases in the same direction as shown below (negative charges carried by the anions are given in parentheses):  $C^{4-}(-4) > N^{3-}(-3) > O^{2-}(-2) > F^{-}(-1)$ 

**Example.** The covalent character of Be<sup>2+</sup>–Cl<sup>-</sup>, Mg<sup>2+</sup>–Cl<sup>-</sup>, Ca<sup>2+</sup>–Cl<sup>-</sup>, Sr<sup>2+</sup>–Cl<sup>-</sup> and Ba<sup>2+</sup>–Cl<sup>-</sup> bonds in BeCl<sub>2</sub>, MgCl<sub>2</sub>, CaCl<sub>2</sub>, SrCl<sub>2</sub> and BaCl<sub>2</sub> molecules *decreases* in the following order :

 $Be^{2+}-Cl^- > Mg^{2+}-Cl^- > Ca^{2+}-Cl^- > Sr^{2+}-Cl^- > Ba^{2+}-Cl^-,$ 

since the polarising power (or size) of  $Be^{2+}$ ,  $Mg^{2+}$ ,  $Ca^{2-}$ ,  $Sr^{2+}$  and  $Ba^{2+}$  cations (*cations of the same group*) to polarise  $Cl^-$  anion *increases* in the same direction as shown below :

 $Be^{2+}(0.31 \text{ Å}) < Mg^{2+}(0.65 \text{ Å}) < Ca^{2+}(0.99 \text{ Å}) < Sr^{2+}(1.13 \text{ Å}) < Ba^{2+}(1.35 \text{ Å})$ 

Due to maximum polarising power (or smallest size) of  $Be^{2+}$  ion, it forms largely covalent bond with  $Cl^-$  ion or with any other anion while other cations of IIA group form largely ionic bonds, *i.e.*  $BeCl_2$  is largely covalent while other chlorides are largely ionic.

**3.** Size of the anion should be large. Larger the size of the anion, more strongly or easily it will be polarised by a given cation, *i.e.* more will be its polarisability and hence greater will be the tendency of the anion to form covalent compounds.

**Examples** (a) The covalent character of  $Ca^{2+}-F^-$ ,  $Ca^{2+}-Cl^-$ ,  $Ca^{2+}-Br^-$  and  $Ca^{2+}-I^-$  bonds in  $CaF_2$ ,  $CaCl_2$ ,  $CaBr_2$  and  $CaI_2$  molecules respectively increases in the following order :

 $Ca^{2+}-F^- < Ca^{2+}-Cl^- < Ca^{2+}-Br^- < Ca^{2+}-I^-$ 

since the polarisability or size of  $F^-$ ,  $Cl^-$ ,  $Br^-$  and I anions (anions of the same group) to be polarised by  $Ca^{2+}$  cation also *increases* in the same direction as shown below:

 $F^{-}(1.36 \text{ Å}) < Cl^{-}(1.81 \text{ Å}) < Br^{-}(1.95 \text{ Å}) < I^{-}(2.16 \text{ Å})$ 

 $F^-$  anion has so small polarisability or size that  $CaF_2$  is *largely ionic* in nature while other halides of  $Ca^{2+}$  are largely *covalent in character*.

(b) Similarly the covalent character of Na<sup>+</sup>-F<sup>-</sup>, Na<sup>+</sup>-Cl<sup>-</sup>, Na<sup>+</sup>-Br<sup>-</sup> and Na<sup>+</sup>-I<sup>-</sup> bonds in NaF, NaCl, NaBr and NaI molecules respectively increases in the following order :

 $Na^+-F^- < Na^--Cl^- < Na^+-Br^- < Na^+-I^-$ 

(c) On similar grounds it can be shown that the covalent character of halogen acids viz. HF, HCl, HBr and HI containing the anions of the same group is in the order :

HF < HCl < HBr < HI

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(d) Due to the increase in polarisation of X<sup>-</sup> anion by  $Al^{3+}$  cation from F<sup>-</sup> to I<sup>-</sup> or due to the increase of the size of the anions from F<sup>-</sup> to I<sup>-</sup>, the covalent character of the trihalides of Al is in the order :

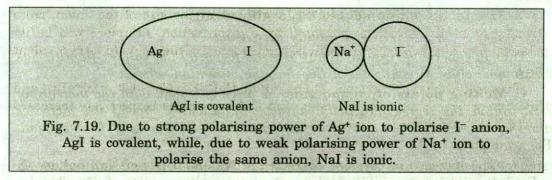
$$AIF_3 < AlCl_3 < AlBr_3 < AlI_3$$

Thus  $AlI_3$  and  $AlBr_3$  have largely covalent character,  $AlCl_3$  has intermediate character while  $AlF_3$  has largely ionic character.

4. Cation should have 18 electron valence-shell configuration  $(ns^2p^6d^{10} configuration)$ . The cation with  $ns^2p^6d^{10}$  configuration has greater polarising power than the cation with 8-electron valence-shell configuration  $(ns^2p^6 configuration)$  and hence has greater tendency to form covalent compound.

**Examples** (a)  $Cu^+-Cl^-$  bond is CuCl is more covalent than Na<sup>+</sup>-Cl<sup>-</sup> bond in NaCl, since  $Cu^+$  has  $3s^2p^6d^{10}$  configuration while Na<sup>+</sup> has  $2s^2p^6$  configuration. Due to 18-electron valence-shell configuration,  $Cu^+$  ion has greater polarising power to polarise  $Cl^-$  ion than Na<sup>+</sup> ion having 8-electron valence-shell configuration.

(b) Due to the 18-electron valence-shell configuration  $(4s^2p^6d^{10})$ , the polarising power of Ag<sup>+</sup> ion to polarise I<sup>-</sup> ion in AgI molecule is so great that it makes AgI *covalent* while, due to 8-electron configuration  $(2s^2p^6)$ , the polarising power of Na<sup>+</sup> ion to polarise I<sup>-</sup> ion in NaI molecule is so small that it makes NaI *ionic*. (See Fig. 7.19).



**B.** Solubility of compounds in non-polar (organic) and polar solvents. As already stated, with the increase of polarisation, the degree of covalent character in an ionic molecule increases. This increase in covalent character is accompanied by an increase of the solubility of the compound in non-polar (organic) solvents like alcohol, but its solubility in polar solvents like  $H_2O$  decreases with the increase in covalent character. For example :

(i) Since the polarisability of S<sup>2-</sup> anion to be polarised by a metallic cation, say, M<sup>+</sup> is greater than that of O<sup>2-</sup> anion, M<sup>+</sup>-S<sup>2-</sup> bond has more covalent character than M<sup>+</sup>-O<sup>2-</sup> bond in M<sub>2</sub>S and M<sub>2</sub>O molecules respectively. With the increase of covalent character in M<sub>2</sub>S, M<sub>2</sub>S is more soluble than M<sub>2</sub>O in non-polar (organic) solvents like alcohol etc. but less so in polar solvents like H<sub>2</sub>O. Thus in general sulphides are less soluble in water than the oxides of the same metal.

(ii) Li<sup>+</sup> cation has the maximum polarising power of all the alkali metal cations and hence gives *largely covalent compounds* while other alkali metal

cations give *largely ionic compounds*. With the increase of covalent character in  $Li^+$  compounds these are readily soluble in non-polar (organic) solvents like alcohol but insoluble in polar solvents like H<sub>2</sub>O, while the compounds of other alkali metal cations are insoluble in organic solvents but readily soluble in polar solvents like H<sub>2</sub>O.

(*iii*) On similar grounds, it can explained why the compounds of  $Be^{2+}$  are insoluble in  $H_2O$  while the compounds of other alkaline earth metal cations are readily soluble in  $H_2O$ .

(iv) We know that CuX, AgX, and AuX halides (X = Cl, Br and I) are much more covalent in nature than the halides of alkali metal cations having similar size and charge as Cu<sup>+</sup>, Ag<sup>+</sup> and Au<sup>+</sup> ions. Due to the increased covalent character, CuX, AgX and AuX are insoluble in water while the alkali metal halides are freely soluble.

(v) We have already seen that the covalent character of the halides of  $Al^{3+}$  increases from  $AlF_3$  to  $AlI_3$ .

### $AlF_3 < AlCl_3 < AlBr_3 < AlI_3$

- Covalent character increasing  $\rightarrow$ 

With the increase of covalent character from  $AlF_3$  to  $AlI_3$ , solubility of these halides in polar solvents like  $H_2O$  decreases in the same direction as shown below :

$$AlF_3 > AlCl_3 > AlBr_3 > AlI_3$$
  
- Solubility decreasing  $\rightarrow$ 

Thus in general we can say that if a metal forms all the halides, fluoride has maximum solubility while the iodide has the minimum solubility.

**C. Melting points of compounds.** As already stated, with the increase of polarisation, the degree of covalent character in an ionic compond also increases and this increased covalent character decreases the melting point of the compound. For example :

(i) The increase in covalent character in  $Na^+-X^-$  bonds of NaX halides (X = F, Cl, Br and I) from NaF to NaI decreases the melting points of these halides in the same direction as shown below :

Halides	:	NaF		NaCl		NaBr		NaI
Covalent character of Na <sup>+</sup> – X <sup>-</sup> bond	}:	Na <sup>+</sup> - F <sup>-</sup>	<	Na+ – CF	<	Na <sup>+</sup> - Br	- <	Na+ - I-
Melting point (°C)		988	>	801	>	755	>	651
								** 1 1.1

Similarly the increase in covalent character in  $Ca^{2+}-X^{-}$  bonds of  $CaX_{2}$  halides (X = F, Cl, Br and I) from  $CaF_{2}$  to  $CaI_{2}$  decreases the melting points of these halides in the same direction as shown below :

Halides	est i pa	$CaF_2$	INT N	CaCl		CaBr <sub>2</sub>		CaI2	
Covalent character of Ca <sup>2+</sup> – X <sup>-</sup> bona	$\left\{ \right\} : $	$Ca^{2+} - X$	- < (	Ca <sup>2+</sup> – C.	t < 0	$Ca^{2+} - B$	r-< 1	Ca <sup>2+</sup> – F	
Melting point (°C)	:	1392	>	772	>	730	>	575	

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(*ii*) The decrease in covalent character in  $M^{2+}$ -Cl<sup>-</sup> bond ( $M^{2+} = Be^{2+}$ ,  $Mg^2$ , Ca<sup>2+</sup>, Sr<sup>2+</sup>, Ba<sup>2+</sup>) of MCl<sub>2</sub> chlorides from BeCl<sub>2</sub> to BaCl<sub>2</sub> increases the melting points of these chlorides in the same direction.

Chlorides	:	BeCl2	MgCl2	CaCl2	SrCl <sub>2</sub>	BrCl <sub>2</sub>
Covalent	antella A	ert. juite				1. 1. 1. 1. 11. 11. 13 S
character	Line	1	at Date Sala	the states	the laboration of the	miles when
of	: .	$Be^{2+} - CT$	$> Mg^{2+} - Ct >$	$a Ca^{2+} - Ct$	$> Sr^{2+} - Ct >$	$a^{2+} - Ct^{-}$
Mar - Cr bond	serf 1	et intermeta	apina on m	unituri nu te	states of adapt	1. 1 160
j oona j			1812 51 5 4 7 7 7		and an and the s	12 - Louis Bearing

Melting point (°C): 405 < 712 < 772 < 872 < 960

(*iii*) We have seen that in NaCl,  $MgCl_2$  and  $AlCl_3$  molecules the covalent character of the bond increases from Na<sup>+</sup>-Cl<sup>-</sup> to  $Mg^{2+}$ -Cl<sup>-</sup> to  $Al^{3+}$ -Cl<sup>-</sup>. This successive increase in the covalent character of the bond decreases the melting points of these chlorides in the same direction as shown below :

Chlorides	: NaCl	MgCl <sub>2</sub>	AlCl <sub>3</sub>
Covalent character of M – Cl (M = Na, Mg, Al bond	• : Na <sup>+</sup> - Cl <sup>-</sup> <	Mg <sup>2+</sup> - Ct <	Al <sup>8+</sup> - Cl <sup>-</sup>
Melting point (°C)	. 800 >	712 >	Sublimes

(*iv*) We know that since  $\text{Sn}^{4+}-\text{Cl}^-$  bond in  $\text{SnCl}_4$  has more covalent character than  $\text{Sn}^{2+}-\text{Cl}^-$  bond in  $\text{SnCl}_2$ ,  $\text{SnCl}_4$  has less melting point than  $\text{SnCl}_2$ , ( $\text{SnCl}_4 = -33^{\circ}\text{C}$ ,  $\text{SnCl}_2 = 246^{\circ}\text{C}$ ).

Similarly PbCl<sub>4</sub> which has greater covalent character than PbCl<sub>2</sub> has less melting point (PbCl<sub>4</sub> =  $-15^{\circ}$ C, PbCl<sub>2</sub> =  $501^{\circ}$ C). TlCl<sub>3</sub> has more covalent character than TlCl and hence has less melting point (TiCl<sub>3</sub> =  $25^{\circ}$ C, TlCl =  $430^{\circ}$ C).

(v) Due to the presence of  $Cu^+$  cation with  $ns^2p^6d^{10}$  configuration, CuCl has more covalent character than NaCl which has Na<sup>+</sup> cation with  $ns^2p^6$  configuration. CuCl has, therefore, less melting point than NaCl (CuCl = 422°C, NaCl = 801°). Other such examples with their melting points are :

**D.** Cause of diagonal relationship. The cause of diagonal relationship can also be explained on the basis of the concept of polarisation of ions as follows :

We have seen that on moving from left to right in a period the positive charge on cations increases and their size decreases. Both these factors increase the polarising power of the cations in a period. However, on moving down a group, the positive charge on the cations remains the same but the size of the cations increases. The increase in the size decrease the polarising power of the cations. On moving diagonally in the periodic table, these two effects partly cancel each other and a good similarity in properties of the two members of a diagonal pair is observed.

**Summary of Fajans's Rules** 

Whatever has been studied so for reveals that Fajans's rules can be summarised by saying that the conditions which bring about maximum polarisation of the anion,  $A^-$  by the cation,  $C^+$  in  $C^+A^-$  molecule or which create covalent character in  $C^+-A^-$  ionic bond in  $C^+A^-$  molecule are :

1. The charge either on cation or on anion should be large. The following examples illustrate this point.

(a) The covalent character of LiCl,  $BeCl_2$ ,  $BCl_3$  and  $CCl_4$  molecules containing the cations of the same period (2nd period) is in the order :

$$LiCl < BeCl_2 < BCl_3 < CCl_4$$

(b) The covalent character of  $GeCl_2$ ,  $GeCl_4$ ;  $SnCl_2$ ,  $SnCl_4$  and  $PbCl_2$ ,  $PbCl_4$  pairs is in the order :

 $GeCl_4 > GeCl_2$   $SnCl_4 > SnCl_2$  $PbCl_4 > PbCl_2$ 

(c) The covalent character of  $CH_4$ ,  $NH_3$ ,  $H_2O$  and HF molecules containing the anions of the same period (2nd period) is in the order :

$$CH_4 > NH_3 > H_2O > HF$$

2. The size of the cation should be small. The covalent character of  $BeCl_2$ ,  $MgCl_2$ ,  $CaCl_2$ ,  $SrCl_2$  and  $BaCl_2$  molecules containing the cations of the same group (IIA group) is in the order :

 $BeCl_2 > MgCl_2 > CaCl_2 > SrCl_2 > BaCl_2$ 

3. The size of the anion should be large. The following examples may be studied.

(a) The covalent character of  $CaF_2$ ,  $CaCl_2$ ,  $CaBr_2$  and  $CaI_2$  containing the anions of the same group (VIIA group) is in the order :

 $CaF_2 < CaCl_2 < CaBr_2 < CaI_2$ 

(b) The covalent character of halogen acids namely HF, HCl, HBr and HI containing the anions of the same group (VIIA group) is in the order :

4. The cation should have 18-electron valence-shell configuration. The following examples are worth noting.

(a) CuCl is more covalent than NaCl.

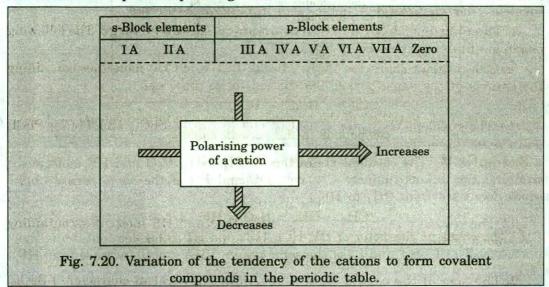
(b) AgI is covalent while NaI is ionic.

Variation of the Tendency of Cations and Anions to Form Covalent Compounds in the Periodic Table

The tendency of a given cation to form covalent compounds depends on the magnitude of its polarising power. Greater is its polarising power, greater is its tendency to give covalent molecule. Further, we have already seen that the

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polarising power of a cation or a given element increases when we proceed from left to right in a period of the long form of periodic table while the same decreases on descending a group. Thus with the increase of the polarising power of a cation from left to right in a period, its tendency to form covalent compounds also increases in the same direction in a period. Similarly with the decrease of the polarising power of a cation from top to bottom in a group, its tendency to form covalent compounds also decreases in the same direction in a group. This variation has been shown pictorially in Fig. 7.20.



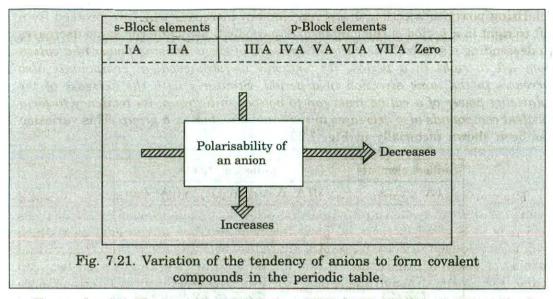
**Examples** (a) The covalent character of LiCl,  $BeCl_2$ ,  $BCl_3$  and  $CCl_4$  molecules containing the cations (namely Li<sup>+</sup>,  $Be^{2+}$ ,  $B^{3+}$  and  $C^{4+}$ ) of the same period (2nd period) increases from LiCl to  $CCl_4$ .

 $LiCl < BeCl_2 < BCl_3 < CCl_4$ 

(b) The covalent character of BeCl<sub>2</sub>, MgCl<sub>2</sub>, CaCl<sub>2</sub>, SrCl<sub>2</sub> and BaCl<sub>2</sub> molecules containing the cations (namely Be<sup>2+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Sr<sup>2+</sup> and Ba<sup>2+</sup>) of the same group (IIA group) decreases from BeCl<sub>2</sub> to BaCl<sub>2</sub>.

 $BeCl_2 > MgCl_2 > CaCl_2 > SrCl_2 > BaCl_2$ 

The tendency of an anion to form covalent compounds depends on the magnitude of its tendency to be polarised by a given cation, *i.e.* on its polarisability. Greater is its polarisability, greater is its tendency to give covalent molecule. Further, we have already seen that the polarisability of an anion of a given element decreases when we proceed from left to right in a period of the long from of periodic table while the same increases on descending a group. Thus with the decrease of the polarisability of an anion from left to right in a period, its tendency to form covalent compounds also decreases in the same direction in a period. Similarly with the increase of the polarisability of an anion from covalent compounds also increases in the same direction in a group. This variation has been shown pictorially in Fig. 7.21.



**Examples** (a) The covalent character of CH<sub>4</sub>, NH<sub>3</sub>, H<sub>2</sub>O and HF molecules containing the anions (namely C<sup>4-</sup>, N<sup>3-</sup>, O<sup>2-</sup> and F<sup>-</sup>) of the same period (2nd period) decreases from CH<sub>4</sub> to HF.

$$CH_4 > NH_3 > H_2O > HF$$

(b) The covalent character of HF, HCl, HBr and HI molecules containing the anions (*viz.*  $F^-$ , Cl<sup>-</sup>, Br<sup>-</sup> and I<sup>-</sup>) of the *same group* (VIIA group) increase from HF to HI.

# Co-ordinate Bond : Bonding by One-sided Sharing of Electrons or Bonding by Electron Pair Donation

#### What is Co-ordinate Bond?

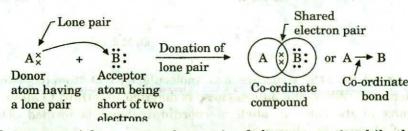
We have seen that in the formation of a normal covalent bond each of the two bonded atoms contributes one electron for the shared pair of electrons which form a covalent bond between the two atoms. However in some compounds the formation of a covalent bond between two atoms takes place by the mutual sharing of two electrons both of which are provided entirely by one of the bonded atoms. This bond is called coordinate bond. Thus :

A covalent bond which is formed by the mutual sharing of two electrons both of which are provided entirely by one of the linked atoms (or ions) is called a coordinate bond.

Co-ordinate bond is also sometimes referred to as *co-ordinate covalent bond* or dative bond. The pair of shared electrons is called *lone pair*. The atom which furnishes the electron pair is called *donor* or *ligand* while the other atom which accepts the electron pair is called *acceptor*. A coordinate bond is represented by an arrow which points away from the donor to the acceptor.

#### Illustration of the Formation of a Coordinate Bond.

The formation of a co-ordinate bond between two atoms, say A and B, can be illustrated as :



The donor atom A has a spare lone pair of electrons on it while the acceptor atom B is short of two electrons than the octet in its valence-shell. A donates its lone pair to B which accepts it. Thus the two electrons of the lone pair which originally belonged to A atom are now shared by both the atoms and this mutual sharing of electron pair results in the formation of a co-ordinate bond between A and B (A  $\rightarrow$  B). Although the arrow head indicates the origin of electrons, once a co-ordinate bond has been established, it becomes quite identical with a normal covalent bond. Both are established by a shared electron pair and have similar properties.

#### Conditions for the Formation of a Co-ordinate Bond.

Conditions which are necessary for the formation of a coordinate bond are :

(i) The atom acting as a donor should have a lone pair of electrons.

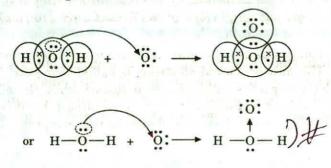
(*ii*) The atom acting as an acceptor should have a vacant orbital to accept the electron pair donated by the donor.

Writing the Electronic Formulae (Lewis Formulae) of the Compounds or Ions Having Co-ordinate Bonds

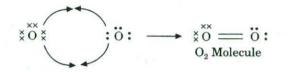
The compounds which contain coordinate bonds are called co-ordinate compounds. Some of them are given below :

 $H_2O_2$  molecule. This molecule can be regarded as being formed by the combination of H<sub>2</sub>O molecule and oxygen atom. Oxygen atom of H<sub>2</sub>O molecule has two lone pairs of electrons on it.

In the formation of  $H_2O_2$  molecule by the combination of  $H_2O$  molecule and oxygen atom, one of the two lone pairs on oxygen atom of  $H_2O$  molecule is donated to the new oxygen atom and thus a coordinate bond is established between oxygen atom of  $H_2O$  molecule and the new oxygen atom.



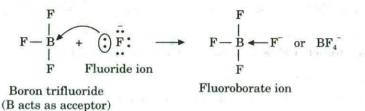
**2.**  $O_3$  molecule. We know that  $O_2$  molecule is made up of two O-atoms which are joined together by covalent bonds.



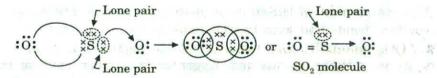
As is evident from the structure of  $O_2$  molecule, each O-atom has two unshared pairs of electrons. When one pair of these is donated to a third O-atom which has six electrons in its valence- shell, a coordinate bond is formed. Thus Lewis structure of  $O_3$  may be shown as :

$$\overset{\times\times}{_{\times}^{\times}}_{O_2} = \ddot{O} \bigcirc + \dot{O} : \longrightarrow \overset{\times\times}{_{\times}^{\times}}_{O_3} = \ddot{O} \longrightarrow \ddot{O} : )$$

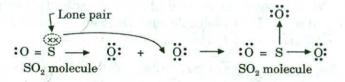
**3. Fluoroborate ion, BF\_4**. It is formed when  $BF_3$  molecule shares a pair of electrons supplied by  $F^-$  ion.



4.  $SO_2$  and  $SO_3$  molecules. Sulphur achieves its octet by forming two covalent bonds with one O-atom, giving SO species. The S-atom in SO has two lone pairs, one of which is shared with a second O-atom to form  $SO_2$ .

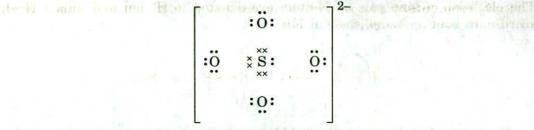


S-atom in  $SO_2$  still has one lone pair which it donates to a third O-atom forming  $SO_3$  molecule.

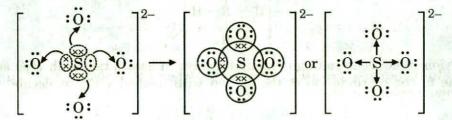


5.  $SO_4^{2-}$  ion. Due to the presence of two negative charges on the ion, S-atom which has six electrons in its valence-shell (2, 8, 6) gains two additional electrons from the metal ion to complete its octet. Thus in  $SO_4^{2-}$  ion, S-atom has eight electrons (four pairs of electrons)-six of its own and two gained from metal ion.

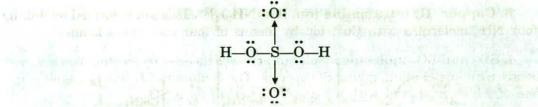
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Now the four electron pairs round S-atom in  $SO_4^{2-}$  ion are donated to four O-atoms each of which thus achieves its octet. Thus we see that S-atom is linked with four O-atoms by four co-ordinate bonds.



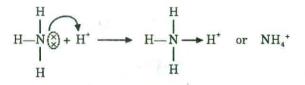
Here it may be noted that Lewis structure of  $H_2SO_4$  is different from that of  $SO_4^{2-}$  ion as shown below.



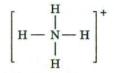
Thus we see that in  $H_2SO_4$  molecule S-atom is linked with two O-atoms by two covalent bonds and with two O-atoms by two co-ordinate bonds.

**6.** CO molecule. C-atom has four valence-electrons (2, 4) while O-atom has six (2, 6). By forming two covalent bonds between them, O-atom achieves octet but C-atom has only six electrons. Therefore O-atom donates an unshared electron pair to C-atom and a coordinate covalent bond is established between the two atoms. Thus CO has two covalent bonds and one coordinate bond  $(O \rightarrow C \text{ bond})$ .

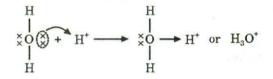
7. Ammonium  $(NH_4^+)$  and hydroxonium  $(H_3O^+)$  ions.  $NH_4^+$  ion may be regarded as being obtained by the combination of  $NH_3$  molecule and  $H^+$  ion. In  $NH_3$  molecule each of the three H-atoms is linked to N-atom by a covalent bond. Thus N-atom in this molecule is left with a lone pair of electrons after completing its octet by sharing three of its five valence-shell electrons with three H-atoms. The electrons of lone pair on N-atom are donated to  $H^+$  ion and thus a  $N \rightarrow H$  coordinate bond is established in  $NH_4^+$  ion.



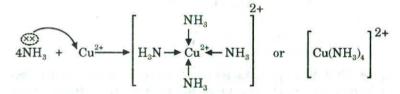
However, after the formation of  $NH_4^+$  ion all the four N-H bonds become identical and hence  $NH_4^+$  ion is represented as shown in the margin.



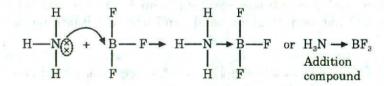
 $H^+$  ion in aqueous solution is found always in association with  $H_2O$  as  $H_3O^+$  ion due to the coordination of the  $H^+$  ion with neutral water molecule.



8. Copper (II) tetrammine ion,  $[Cu(NH_3)_4]^{2+}$ . This ion is formed by linking four NH<sub>3</sub> molecules with Cu<sup>2+</sup> ion by means of four coordinate bonds.



**9.** Addition compounds. Coordinate bond is also formed between two atoms both of which are the parts of a stable molecule. For example this type of bond is found in boron *fluoride-ammonia complex*,  $H_3N \rightarrow BF_3$ .

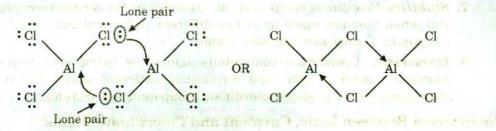


Addition compounds are generally represented by placing a dot between the formulae of their constituent molecules, e.g. NH<sub>3</sub>. BF<sub>3</sub>.

10. Aluminium chloride,  $A1_2Cl_6$ . Al atom has three valence-electrons which it shares with three Cl-atoms, forming three covalent bonds. Thus in AlCl<sub>3</sub>, Al atom acquires six electrons in its outershell. Now each of the three Cl-atoms in AlCl<sub>3</sub> molecule has three lone pairs. One of these lone pairs is donated to Al

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atom of another  $AlCl_3$  molecule. Thus both Al atoms achieve an octet and a stable  $Al_2Cl_6$  molecule results.



# How is a Co-ordinate Bond Formed ?

The formation of a coordinate bond  $(A \rightarrow B)$  between two atoms *viz*. A and B may be regarded to occur in the following two steps :

1st step: In this step the donor atom A transfers one electron of its lone pair to the acceptor atom B. This results in that atom A develops *unit positive charge* (+) and atom B develops a *unit negative charge* (-). This charge is known as *formal charge*. This step is similar to the formation of an ionic bond.



**2nd step :** In this step the two electrons, one each with  $A^+$  and  $B^-$  are shared by both the ions. This step is similar to the formation of a covalent bond.

 $A^{\bullet^+} + \bullet B^- \rightarrow A : B \quad or \quad A \rightarrow B$ 

Thus we see that a co-ordinate bond is equivalent to a combination of an electrovalent bond (polar bond) and a covalent bond (non-polar bond). It is for this reason that a coordinate bond is also sometimes called a *semi-polar bond*.

#### **Properties of Co-ordinate Compounds.**

The main characteristics are given below :

- 1. *Melting / boiling points and viscosity.* We have seen that a co-ordinate bond is, in a way, a combination of an ionic bond and a covalent bond. It is for this reason that coordinate compounds have melting and boiling points, and viscosities which are *higher* than those of purely covalent compounds but *lower* than those of purely ionic compounds.
- **2.** Semi-polar character. These compounds are semi-polar in character  $(A^+-B^-)$ , *i.e.* they are more polar than covalent compounds and less polar than the ionic compounds.
- 3. Physical state. These compounds are gases, liquids or solids.
- 4. Solubility. These are usually insoluble in polar solvents like water but are soluble in non-polar (*i.e.* organic) solvents.
- 5. Conductivity. Like covalent compounds, coordinate compounds are also non-ionic, i.e. they do not conduct electric current through their aqueous solutions or fused mass.

- 6. *Molecular reactions*. Coordinate compounds are molecular and hence undergo molecular reactions which are slow.
- 7. Stability. Coordinate compounds are as stable as the covalent compounds. But when they are made up of two different stable molecules (*molecular* compounds), they are not very stable.
- 8. Isomerism. Coordinate compounds also show isomerism. Since the coordinate bond is *rigid* and *directional*, different space models (*i.e.* stereoisomers) of a single coordinate compound are possible.

#### **Comparison Between Ionic, Covalent and Co-ordinate Bonds**

The comparison between the three bonds is given in Table 7.2.

#### Table 7.2. Comparison between ionic, covalent and co-ordinate bonds

Ionic Bond	Covalent Bond	Coordinate Bond			
(i) Ionic bond is formed by the transfer of electrons from a metal atom (A) which has 1, 2 or 3 valence-electrons to a non-metal (B) having 5, 6 or 7 valence electrons.	(i) Covalent bond is formed by sharing two electrons between non-metal atoms having 1, 4, 5, 6, or 7 valence electrons.	(i) It is formed by the sharing of two electrons between two atoms, both electrons coming from one atom.			
$A \times + \cdot \ddot{B} : \rightarrow [A] + \left[ \dot{\times} \ddot{B} : \right]$ or $A + B^-$	$\begin{array}{c} \overset{x\times}{\underset{x\timesx}{\overset{x}{\underset{x\timesx}{\overset{x}{\underset{x\timesx}{\overset{x\timesx}{\underset{x\timesx}}{\overset{x\timesx}{\underset{x\timesx}}{\overset{x\timesx}{\underset{x\timesx}{\overset{x\timesx}{\underset{x\timesx}{\overset{x\timesx}{\underset{x\timesx}}{\overset{x\timesx}{\underset{x\timesx}}{\overset{x\timesx}{\underset{x\timesx}}{\overset{x\timesx}{\underset{x\timesx}}{\overset{x\timesx}{\underset{x\timesx}}{\overset{x\timesx}{\underset{x\timesx}}{\overset{x\timesx}{\underset{x\timesx}}{\overset{x\timesx}{\underset{x\times}}}{\overset{x\timesx}{\underset{x\times}}}}{\overset{x\timesx}{\underset{x\times}}}}}}}}}}}}}}}$	$\begin{array}{c} \stackrel{\times}{}_{XX}^{XX} \stackrel{\times}{}_{XX} \stackrel{H}{}_{X} \stackrel{H}{}_{$			
( <i>ii</i> ) Ionic bond con- sists of electrostatic force between cations and anions.	( <i>ii</i> ) Covalent bond consists of two electrons that hold the atoms together.	( <i>ii</i> ) It consists of an electron pair between the linked atoms.			
( <i>iii</i> ) It is a weak bond, since the electro-static force can be broken easily.	( <i>iii</i> ) It is a strong bond, since the paired electrons cannot be separated easily.	( <i>iii</i> ) It is also a strong bond, since the paired electrons cannot be sepa- rated easily.			
(iv) It is a polar bond $(A^+-B^-)$	(iv) It is a non-polar bond (A-B)	(iv) It is a semi-polar bond $(A^+ - B^-)$			

### **Metallic Bond**

#### What is Metallic Bond?

Since all the atoms in a metal crystal are identical, these cannot be linked by ionic bonds as cations and anions are bonded together in ionic crystals, Moreover, ionic bond cannot be formed between the metal atoms, since the metal atoms have the same electronegativities.

Also, each atom in a metal crystal cannot be bonded to other 8 or 12 atoms (X-ray study of metal crystals has shown that each metal atom is surrounded by

8 or 12 other metal atoms) by the covalent bond (sharing of electrons), since in metals the number of valence electrons is insufficient for the formation of covalent bonds with all its 8 or 12 neighbouring metal atoms. For example Na atom which has only one valence electron cannot be expected to form covalent bonds with 8 nearest neighbouring Na atoms in its crystal.

Obviously, the metal atoms in a metal crystal are bonded together by a bond which is neither an ionic bond nor a covalent bond, but it is a special type of bond which is called *metallic bond*. This bond binds the metal atoms together in a metal crystal and is of its own type.

HThe peculiar type of bonding which holds the metal atoms together in a metal crystal is called metallic bonding.

## To Explain the Nature of Metallic Bond by Electron-Gas Theory

In order to explain how the metal atoms in a metal crystal are bonded together, a simple theory, first proposed by Drude (1900) and later on developed by Lorentz (1916), is known as *electron-cloud* or *electron-pool* or *electron-gas theory*. This theory can well explain the nature of forces holding the metal atoms together in a metal crystal (Metallic bond).

Since the ionisation energies of metals are low, they readily give up their valence electrons to form the metal ions (called *positive cores or kernels*). The electrons given by the metal atoms move from place to place through the empty valence orbitals of the closed packed metal ions and are shared simultaneously by all the atoms together by a characteristic type of bond which is called *metallic bond*.

The electrons now no longer belong to individual metal atoms but belong to the crystal as a whole. As a result of delocalisation of electrons, the positive metal ions that are produced, remain fixed in the crystal lattice while the delocalised electrons move freely in the vacant valence orbitals. Thus on the basis of this theory :

A metal is regarded as a group of positive metal ions packed together as closely as possible in a regular geometric pattern and immersed in a sea of electrons (called electron-pool or electron-gas or electron-cloud) which move about freely (mobile or delocalised electrons) in the vacant valence orbitals. The attractive force that binds the metal ions to the mobile electrons is called **metallic bond** and the force of attraction between the metal ions and the mobile electrons holds the atoms together.

The electrons which are moving from place to place through the space between the metal ions are called *electron-gas* because of their mobile nature.

Diagrammatic representation of metallic bond in sodium metal is shown in Fig. 7.22. Circles with + sign at the centre represent Na<sup>+</sup> ions (positive metal cores) and - sign represents an electron. Attraction between the positive metal cores and mobile electrons has been shown by arrows and this constitutes the metallic bond.

The bonding which holds the metal atoms firmly together as a result of the attraction between the positive metal ions and surrounding freely mobile electrons, is called the **metallic bonding**.

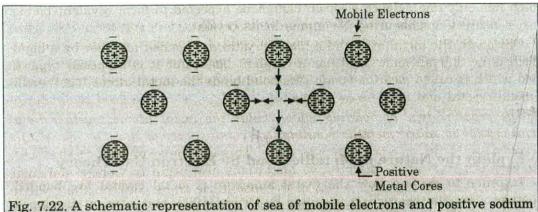
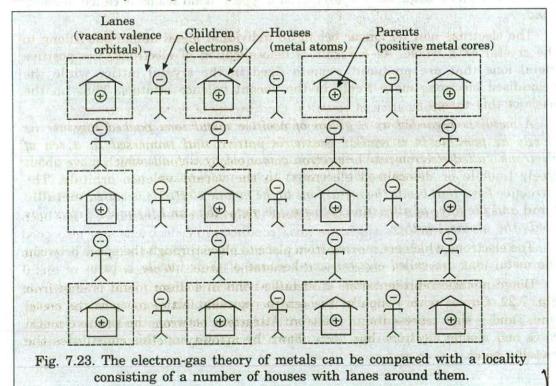


Fig. 7.22. A schematic representation of sea of mobile electrons and positive sodium metal cores. The attraction between the positive metal sodium cores and mobile electrons constitute the metallic bond. (Attraction has been shown by arrows).

The electron-gas model of metals can be compared with a locality consisting of a number of houses with lanes around them (Fig. 7.23). Children (*electrons*) from different houses (*metal atoms*) are free to play or move anywhere in the lanes (*vacant valence orbitals*) within the locality (*structure of the metal*) itself, but are not allowed by their parents (*positive metal cores*) to go away from the locality.

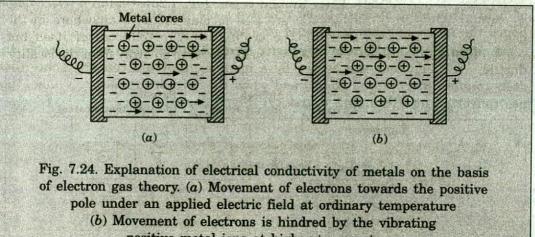


# **Explanation of Physical Properties of Metals**

The electron gas theory of metals can well explain various physical properties of metals. This has been shown as follows :

1. Metals are good conductors of electricity (Electrical conductivity). When an electric field is applied between the two ends of a metal, the mobile electrons begin to move towards the positive pole and the new electrons from negative pole take their position. Thus with the movement of electrons, the electric current starts to flow in the metal and the metal, therefore, acts as a good conductor of electricity [See Fig. 7.24 (a)].

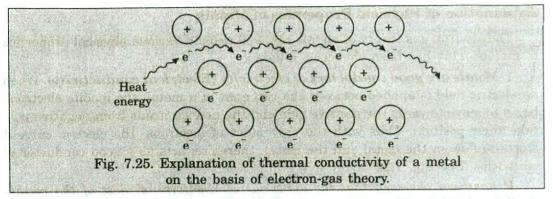
It has been observed that the electrical conductivity of most of the metals decreases with the increase of temperature. This is because of the fact that with increase of temperature the positive metal ions also begin to vibrate and their motion hinders the free movement of the mobile electrons between the positive metal ions [Fig. 7.24 (b)]. Thus the vibrating positive metal cores create resistance to the flow of the electrons towards the positive pole and hence the movement of the electrons towards the positive pole falls and so does the electrical conductivity of the metals at higher temperature.



positive metal ions at higher temperature.

2. Metals are good conductors of heat (Thermal conductivity). It has been observed that the metals which are good conductors of electricity are also good conductors of heat. Thermal conductivity of metals can also be explained on the basis of mobile electrons present is the metallic lattice. When a piece of metal is heated at one end, the mobile electrons at this end absorb heat energy from this end and move very rapidly through the metallic lattice towards the cooler end. During this process they collide with adjacent electrons and thus transfer their heat energy to them (Fig. 7.25). Thus the mobility of electrons allows heat transfer to the other end.

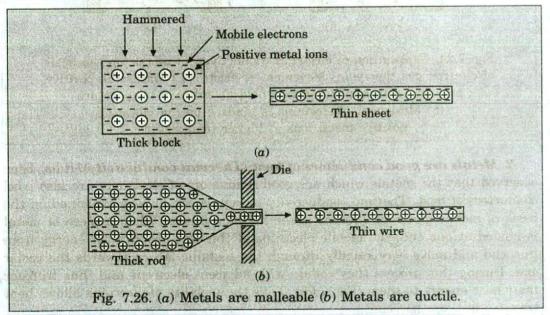
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**3.** Metals are opaque and have lustre or colour. The light that falls on metals is absorbed completely by the electronic transitions of the sea of electrons. Since no light is permitted to pass through the metal, it is opaque.

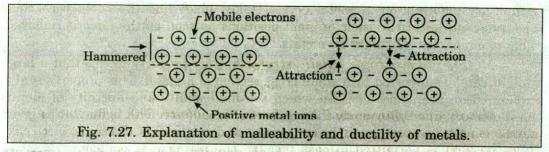
When freshly cut or scratched, most of the metals possess metallic lustre, *i.e.* they have a shining surface. The lustre of metals can also be explained on the basis of mobile electrons. When light falls on the surface of the metal, the incident light collides with the mobile electrons which are excited. When these excited electrons revert to their original position, they give off energy in the form of light. This light appears to be reflected from the surface of the metal and hence the metal appears to possess its characteristic lustre.

4. Metals are malleable or plastic and ductile. Metals are malleable and ductile, *i.e.* when they are beated by a hammer, they are converted into their seets (malleability) [Fig. 7.26 (a)] and when they are drawn through a die, they are converted into thin wire (ductility) [Fig. 7.26 (b)].



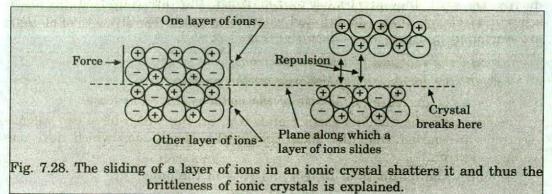
When a metal is beaten, say by a hammer, one layer of positive metal ions moves along another layer through a distance and occupies new positions. Since

the sea of electrons (*i.e.* valence electrons) are mobile, they also move along with the positive metal ions and thus the structure of the metal does not alter but remains the same and the crystal structure is restored (Fig. 7.27). This results in that the thickness of the metal is reduced and the metal is converted into thin sheet or thin wire.

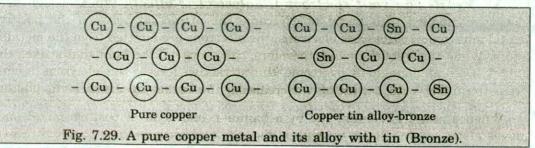


However, if an alloying metal is added to a metal, the structural homogeneity of the principal metal is disturbed and hence the resulting alloy is hard and brittle.

Brittleness of ionic crystals. When a little force is applied on an ionic crystal, the ions in a layer slide a bit over another layer and the ions having similar charges in the two layers come in contact with each other and hence begin to repell each other (Fig. 7.28). The force of repulsion created by this situation shatters the ionic crystal, *i.e. ionic solids are highly brittle*. In case of metals, as we have seen above, this does not happen and hence in this respect the metals differ from the ionic crystals.



5. Metals form alloys. Metallic mixtures are called alloys. Metals form alloys easily. In these alloys, the spherical ions of different metals share the same sea of electrons. (Fig. 7.29).



Only such metals can form the alloys the atoms of which when mixed can fit into the crystal lattice of the other. This is only possible, if the geometry of the mixing atoms allows this fitting in, *i.e.* if the diameter of the atom of one metal is much greater than that of the other, no alloy can be formed by the two metals.

6. Metals have elasticity. Under the influence of comparatively less force, temporary deformation of metal crystal takes place and the cores with their electron-cloud return to their original positions as soon as the force is removed. This explains the elasticity in metals.

7. Metals possess high tensile strength. This property means that a large weight can be supported by a small cross section of a metal. This property is also explained on the same basis on which the malleability and ductility of metals has been explained. Obviously the property of tensile strength is due to the great attraction between the positive metal ions and the mobile electrons.

8. Metals are solids and have high density. Metals are solids (mercury being the only exception) and have high density. The high density is due to the fact that the metallic bond keeps the metal atoms closely packed in the metallic crystal.

**9.** Melting and boiling points. In general, metals have intermediate melting and boiling points as compared to those of covalent and ionic compounds. This is due to the reason that the attractive forces (*i.e.* metallic bonds) that hold the metal atoms together in metallic crystal are intermediate between those in covalent and ionic compounds.

10. Metals are usually hard solids. Because of the strong metallic bonds between the metal atoms, metals are usually hard solids. The strength of metallic bond usually increases

(a) with the increase of valence electrons.

(b) with the increase of the charge on the nucleus.

(c) with the decrease of the size of the metal positive ion (core).

For example the alkaline earth metals (Ca, Sr, Ba) which have two valence electrons are harder than the alkali metals (Li, Na, K etc.) which have one valence-electron.

Similarly the hardness of Li, Na and K is in the order

$$Li > Na > K$$
,

because the size of Li<sup>+</sup>, Na<sup>+</sup> and K<sup>+</sup> ions is in the order :

#### $Li^{+} < Na^{+} < K^{+}$

11. Metals can emit electrons (Photoelectric effect). When enough heat energy is applied to a metal to overcome the attraction between the positive metal ions (metal cores) and electrons, the electrons are emitted from the metallic atom. When the frequency and, therefore, the energy of the light that strikes the metal is great enough to overcome the attractive forces, the electrons escape from the metal with a resultant decrease in the energy of the incident photon. The removal of electrons from the surface of a metal by heat energy is called photoelectric effect.

### Conditions for the Formation of Metallic Bond

The above discussion clearly shows that the metals forming metallic bond should obey the following conditions :

(i) The metals should have *low ionisation energies* so that the metals should readily give up their valence-electrons to form the positive metal ions (cores).

(*ii*) The metals should have vacant valence orbitals so that the positive metal ions may move freely in these vacant orbitals.

### Differences between Metallic and Ionic Bond

(i) Since all the atoms in a metal crystal are similar, there is no possibility of the linking of the metals atoms by ionic bond.

(ii) Further a metal conducts electricity by the motion of electrons from one end to the other. This is quite different from the way in which electrolytes conduct electricity by the migration of their ions. This too confirms that metallic bond differs from ionic bond.

### **Differences between Metallic and Covalent Bond**

(i) Most of the metals have less than four electrons in their valence shell (many metals have only one or two electrons). With so few valence electrons in valence shell, it is not possible for a metal atom to be linked to other eight or twelve atoms (in metal crystal each metal atom is surrounded by 8 or 12 other metal atoms) by sharing the electrons with them and thus attrain the configuration of the nearest inert gas with 8 electrons in its valence shell (*octet rule*). Thus the metal atoms, due to insufficient number of valence electrons, cannot be linked to other metals atoms by covalent bond.

(*ii*) Since the valence electrons in a covalent bond are *localised*, a covalent bond has a *directional character*. On the other hand, since the valence electrons involved in metallic bond are spead all over the metallic crystal, the metallic bond has *non-directional character*.

(*iii*) Further, in covalent bond, due to the presence of localised electrons, there is much more attraction between the valence electrons and the nuclei of the atoms, *i.e.* valence electrons in covalent bond experience strong attractive pull by the nuclei of the atoms. Thus covalent bond is quite strong. On the other hand, in metallic bond, due to the presence of delocalised electrons, (mobile electron) the force of attraction existing between the valence electrons and the nuclei of the atoms is weak, *i.e.* valence electrons in metallic bond are weakly attracted by the nuclei. It is because of this that metallic bond is weaker than a covalent bond. For example the energy required to vaporise a mole of metal like copper to the vapor state is smaller than the energy required to vaporise a mole of metal like graphite.

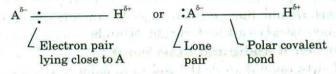
### Hydrogen Bond

#### What is Hydrogen Bond?

In order to understand the concept of hydrogen bond let us consider a molecule, say, AH in which H atom is linked with a *strongly electronegative but very small* 

#### Modern Inorganic Chemistry

atom A (A may be N, O or F) by a normal covalent bond. The electron pair being shared between H and the strongly electronegative atom A will evidently lie far away from H and thus partial positive and negative charges will be developed on H and A atoms respectively. Consequently AH molecule will behave as a dipole which is represented as :



Evidently the dipole has A as its negative end and H as its positive end. Since the electronegative atom, A attracts the electron pair constituting the covalent bond between A and H almost completely towards itself, the atom A takes almost full possession of the electron pair, *i.e.* the atom A will have a lone pair of electrons. This leaves H atom with a large partial positive charge and AH molecule, therefore, becomes highly polar and hydrogen end of it becomes nearly hare hydrogen nucleus or proton (H<sup>+</sup>), *i.e.* H-atom is reduced to a proton which is almost devoid of electrons.

Now if another molecule like AH (same molecule) or BH (different molecule) (A and B are strongly electronegative atoms) which also forms a dipole  $A^{\delta-} - H^{\delta+}$ or  $B^{\delta-} - H^{\delta+}$  respectively is brought near  $A^{\delta-} - H^{\delta+}$  dipole, these two dipoles will be attracted towards each other by electrostatic force of attraction which is represented by a dotted or dashed line and is called hydrogen bond or hydrogen bonding.

Covalent bonds Electrostatic attraction

-Hydrogen bond

interargenti

Hydrogen bond

$$:A^{\delta}-H^{\delta}+:B^{\delta}-H^{\delta}\rightarrow:A^{\delta}-H^{\delta}\in\mathbb{R}^{2} B^{\delta}-H^{\delta} \text{ or } A-H^{\delta}-B-H Covalent bonds -H^{\delta}$$

Thus we see that in H-bond H-atom forms a bridge between two electronegative atoms and for this reason H-bond is also called a H-*bridge*. Thus H-bond can be defined as :

The attractive electrostatic force between a hydrogen atom which is already covalently attached with a strongly electronegative atom of a molecule and another electronegative atom of some other molecule (same molecule or different molecule) is known as hydrogen bond.

OR

Under appropriate conditions a hydrogen atom may be linked to two similar or different electronegative atoms. It is bonded to one of the two atoms by a

covalent bond while to the other atom it is attached by a special type of bond which is much weaker than the covalent bond and is called hydrogen bond.

#### **Nature of Hydrogen Bond**

It is difficult to ascertain the exact nature of hydrogen bond. We know that the covalency of H-atom is limited to one, *i.e.*, H- atom can be linked to only one atom, say A. This is because of the fact that 1s atomic orbital of H-atom becomes completely filled after it has formed a covalent bond, A-H. Thus H-atom already covalently bonded to atom A in A-H bond cannot form a second covalent bond with another atom, say B. This shows that A-H-B in which H-atom shows bivalency is unlikely, because, if it is likely at all, it would require the use of 2sor 2p-orbitals of H-atom which are of much higher energy and consequently are useless for bonding. Further if A-H-B is supposed to be correct, we should expect H-atom to be equidistant from A and B atoms, if the elecnegativities of A and B are the same. However, it has been found by experiments that H-atom in hydrogen bond is close to that atom with which it forms a covalent bond. This shows that hydrogen bond is electrostatic in nature, *i.e.* hydrogen bond is merely an electrostatic force rather than a chemical bond.

A question may now arise as to why H-atom alone is capable of forming hydrogen bond. The reason, probably, is that H-atom has small size with only one electron in its only one energy shell. When this electron is taken away, the proton  $(H^+)$  left behind can easily manage to stap in between two electronegative atoms bringing them closer together by creating an *electrostatic field*, though weak. That is why the proton is in a state of oscillation between the electronegative atoms.

Atoms of sulphur, phosphorus, chlorine, bromine and iodine are also highly electronegative, but they cannot form hydrogen bond. Their incapability is due to their larger atomic size, which results in extremely weak electrostatic field about them.

# **Properties of Hydrogen Bond**

(i) A H-bond is a bond of hydrogen between two electronegative atoms only. It never involves more than two atoms (excluding H-atom).

(*ii*) Bond energy of a H-bond is in the range of 3-10 kcal/ mole while that of a normal covalent bond is in the range of 50-100 kcal/mole. Thus a H-bond (*i.e.*, H...B bond) is much weaker and longer than a covalent bond, A-H and hence it can be readily ruptured. The difference in energy between A-H and H...B bonds indicates that these have different bond lengths which, in turn, show that H-atom in A-H...B is never midway between the two atoms, A and B ; it is rather always nearer to atom A which is covalently bonded to H-atom. Hbond has more energy (= 3-10 kcal/mole) than van der Waals forces (= 1 kcal/ mole).

With the increase of electronegativity of the atom to which H-atom is covalently linked, the strength of H-bond also increases. Thus the strength of H-bonds in N-H...N, O-H...O and F-H...F is in the following order :

Order of strength : N - H...N < O - H...O < F - H...F

Order of electronegativity values : N = 3.0 < O = 3.5 < F = 4.0

The numbers given in brackets indicate the electronegativity values of the elements concerned.

The strength of H-bond also depends on the size of the atom to which H-atom is linked. For example the larger Cl and S atoms whose electronegativities are almost the same as that of N form H-bond to a lesser degree.

(*iii*) The formation of a H-bond does not involve any sharing of electron pairs. It is, therefore, quite different from a covalent bond.

(*iv*) Only O, N and F which have high electronegativity and small atomic size, are capable of forming H-bonds.

(v) Hydrogen bonding results in the formation of long chains or clusters of a large number of associated molecules like as many tiny magnets.

(vi) Like a covalent bond, H-bond has a preferred bonding direction. This is attributed to the fact that H-bonding occurs through p orbitals which contain the lone pair of electrons on A atom. This implies that all the three atoms in A-H...A will be in a straight line.

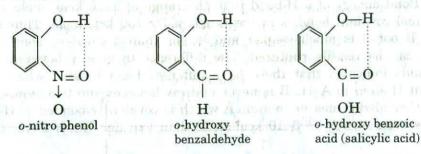
## **Types of Hydrogen Bond**

Hydrogen bond is two types :

**1. Inter-molecular hydrogen bond (Association).** This type of H-bond occurs between two or more molecules of the same or different compound. Thus  $NH_3$ ,  $H_2O$  and HF molecules are associated by inter-molecular H-bond.

2. Intra-molecular hydrogen bond (Chelation). This type of H-bond is formed between a H-atom and an electronegative atom present in the same molecule (*intra* means within). In intramolecular H-bonding, the H-atom is bonded to two atoms of the same molecule. This type of H-bonding may lead to the linking of two groups to form a ring structure and such an effect is one kind of *chelation*. The occurrence of this type of H-bond does not disturb the normal bond angles.

Examples of molecules showing intra-molecular hydrogen bonding are provided by *o*-nitropenol, *o*-hydroxy benzaldehyde, *o*-chlorophenol, *o*-hydroxy benzonic acid (salicylic acid), *o*-nitro benzoic acid, maleic acid etc.



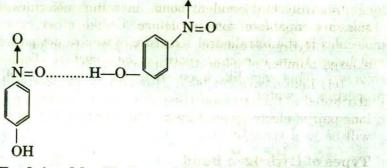
Thus we see that intra-molecular H-bonding in these molecules leads to the formation of a six-membered ring (*chelation*). The occurrence of H-bond of this type is not possible in m-nitrophenol and p-nitrophenol because of the size of the

ring that would result. It is because of the non-existence of H-bond in m- and pisomers that o-nitrophenol has different properties from those of other isomers.
For example :

(i) Melting point of o-nitrophenol is  $214^{\circ}$  while those of its m- and p-isomers are 290° and 279° respectively.

(ii) o-nitrophenol is volatile in steam and less soluble in water than the other two isomers.

*p*-nitrophenol shows inter-molecular H-bonding, resulting in the association of two molecules as shown below.

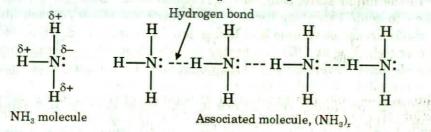


# Physical Properties Explained by Hydrogen Bond — Consequences of Hydrogen Bond.

Some of the unusual properties of the compounds containing H-bond can be explained on the basis of the concept of H-bonding. For example :

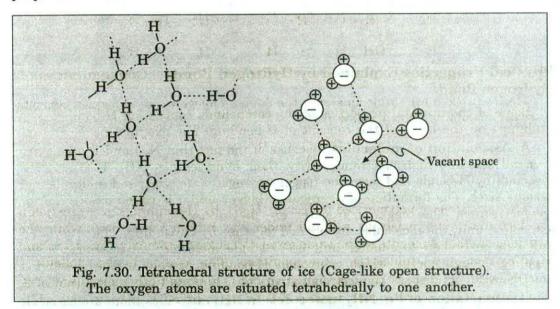
A. Association of molecules. Because of the fact that N,O and F atoms are of small size and high electronegativity, their hydrides viz. NH<sub>3</sub>, H<sub>2</sub>O and HF associate by H-bonds and form the bigger aggregates (polymerised molecules) of various sizes. The formation of aggregates (bigger units) is called *association* or *polymerisation*. The bigger aggregates are *polymerised molecules*. Within the associated unit, the molecules are bonded together by H-bonding. The associated unit can be broken to smaller unit or to single molecules on heating, *i.e.* by suppling enough energy which overcomes H-bonding present in the associated unit. Now let us discuss the association in NH<sub>3</sub>, H<sub>2</sub>O and HF molecules.

(1) Association of liq.  $NH_3$  molecules. In  $NH_3$  molecules there are three Hatoms which are covalently bonded to the highly electronegative N-atom which has a lone pair of electrons on it. This N-atom forms a H-bond with H-atom of the neighbouring  $NH_3$  molecules through its lone pair and gives rise to the formation of an associated molecule,  $(NH)_x$  in the liquid state as shown below :



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(2) Association of H<sub>2</sub>O molecules. (i) Solid state of water (i.e. ice). Here each O-atom of each H<sub>2</sub>O molecule is linked with two H-atoms of its own molecule by covalent bonds and with two H- atoms of the neighbouring H<sub>2</sub>O molecule by H-bonds. Two H-bonds are formed between the two lone pairs of electrons present on O-atom and two H-atoms of the neighbouring H2O molecules as shown in Fig. 7.30. This type of bonding between O-atom and four H-atoms gives a tetrahedral structure to ice. In this structure two H-atoms are linked covalently and lie close to O-atom at a distance of 1.0A° whereas the other two H-atoms (of other H<sub>2</sub>O molecule) are linked by H-bonding and are at a distance of 1.76A° from O-atom. Since the H-bonds joining adjacent H2O molecules are weaker and longer than normal covalent bonds in water molecules, the structure of ice so obtained is cage-like rigid structure. Unlike other crystalline structures, H2O molecules in the tetrahedral structure of ice are not packed very closely together and hence there is vacant space in the structure. Thus, ice has cage-like open structure. This cage-like open structure of ice can well explain the following properties of water :



(a) Liquid water has higher density than solid ice. We have seen that the cage-like open structure of ice has vacant space in it. The presence of vacant space gives a large volume to a given mass of ice. When ice is allowed to melt to come in the liquid state, some of the H-bonds in the cage-like structure of ice are broken to some extent and water molecules come closer to each other. This results in a decrease of volume and hence density is increased. Thus we see that *liquid water* (which is at  $0^{\circ}$ C) has higher density than solid ice while most of the other liquids have lower density than the solids. That liquid water has higher density than solid ice implies that ice is lighter than water.

(b) Ice floats on liquid water. Since ice has lower density than liquid water, ice is lighter than water and hence floats on liquid water.

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(c) Density of water is maximum at 4°C. As the temperature of liquid water  $(= 0^{\circ}C)$  is increased above 0°C, density of water also increases. The increase in density continues only upto 4°C. Above 4°C, kinetic energy of H<sub>2</sub>O molecules increases and hence H<sub>2</sub>O molecules move away from each other, *i.e.* the volume of water molecules is increased. The increase in volume decreases the density of water. Therefore, above 4°C, the density of water starts decreasing again. Thus we see that the density of water is maximum at 4°C.

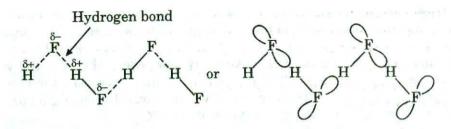
(ii) Liquid state of water. Here each O atom of each  $H_2O$  molecule is covalently linked with two H-atoms of its own molecule and with another Hatom of the adjacent  $H_2O$  molecule by H-bonding. The formation of H-bond occurs through one of the two lone pairs of electrons present on O-atom in  $H_2O$ molecule. The association of different  $H_2O$  molecules by H-bonding gives an associated unit or cluster,  $(H_2O)_x$  which consists of a large number of  $H_2O$ molecules as shown below :

However the most stable cluster is the double molecule,  $(H_2O)_2$  which consists of two H-bonds as shown below :

The formation of polymerised molecule,  $(H_2O)_x$  by H-bonding can well explain the fact that water exists as a liquid under the ordinary conditions while the hydrides of other elements of the same group (VI A group) namely  $H_2S$ ,  $H_2Se$  and  $H_2Te$  exist as gases under the same conditions. This is explained as follows :

Due to the fact that the electronegativity of O-atom is higher than that of S, Se and Te atoms, there is considerable H-bonding in liquid  $H_2O$  molecules while the same is absent in  $H_2S$ ,  $H_2Se$  and  $H_2Te$  molecules. Thus  $H_2O$  molecules can associate to form a *polymerised molecule*.  $(H_2O)_x$  while  $H_2S$ ,  $H_2Se$  and  $H_2Te$ cannot do so. It is due to the formation of polymerised molecule,  $(H_2O)_x$  that water exists as a liquid under the ordinary conditions while  $H_2S$ ,  $H_2Se$  and  $H_2Te$ exist as gases under the same conditions.

(3) Association of HF molecules (i) HF crystals contain infinitely long zigzag chains of HF molecules which are associated to  $(HF)_x$  unit by H-bonding. F atom is covalently bonded to the H-atom of its own molecule while the same atom is bonded to the H- atom of the neighbouring HF molecule by a H-bond. F atom forms H-bond with H-atom of the other HF molecule by its lone pair present in *p*-orbitals. H–F and H...F bond lengths are 1.0Å and 1.55Å respectively.



On heating the length of the chains shortens progressively till the unit,  $(HF)_x$  becomes fairly small and x assumes any value upto six.

(*ii*) Gaseous HF molecule contains molecular species,  $(HF)_2$ ,  $(HF)_3$  and so on upto  $(HF)_6$  as well as some single HF molecules.

(iii) In aqueous solution HF ionises to give  $HF_2^-$  ion (F<sup>-</sup>...H–F) rather than  $F^-$  ion.

**B.** Abnormally high boiling points of  $NH_3$ ,  $H_2O$  and HF hydrides. Let us consider the boiling points of the binary hydrides of the elements of groups VA, VI A and VII A as given below in Table 7.4.

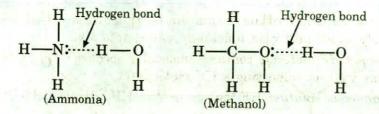
Group VA			Gr	oup VIA		Group VIIA		
Hydride	Mol. wt.	B. pt. (°C)	Hydride	Mol. wt.	B. pt. (°C)	Hydride	Mol. wt.	B. pt. (°C)
SbH <sub>2</sub>	125	-17	H <sub>2</sub> Te	130	-1.8	HI	128	-35.5
AsH3	78	-55	H <sub>2</sub> Se	81	-42.0	HBr	81	-67.1
PHa	34	-85	H <sub>2</sub> S	34	-59.6	HCl	365	-85.0
NH <sub>2</sub>	17	-33	H <sub>2</sub> O	18	100	HF	20	19.4

# Table 7.3. Boiling points of binary hydrides of the element of groups VA, VIA and VIIA

It may be seen from the table that on proceeding from  $SbH_3$  to  $PH_3$  (Group VA), from  $H_2Te$  to  $H_2S$  (Group VIA) and from HI to HCl (Group VIIA), the boiling points of the hydrides decrease with the decrease of their molecular weights while those of  $NH_3$ ,  $H_2O$  and HF show a sudden increase, although they have the minimum molecular weights in their respective groups. The abnormal high boiling points of  $NH_3$ ,  $H_2O$  and HF are due to the fact that these molecules are capable of forming the associated molecules,  $(NH_3)_x$ ,  $(H_2O)_x$  and  $(HF)_x$  by H-bonding between them, while other molecules exist as single molecules as they are incapable of forming associated molecules (clusters) by H-bonding. In order to break H-bonds existing in the associated molecules and thus to separate molecules of the clusters as they enter the gaseous state or the liquid state, relatively more energy is required and hence  $NH_3$ ,  $H_2O$  and HF molecules have abnormally higher boiling points compared to other hydrides of the elements of the same group which do not form any H-bonds.

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C. High solubilities of some covalent compounds. Hydrogen bonding also accounts for the abnormally high solubilities of some covalent compounds containing N, O and F such as  $NH_3$  and  $CH_3OH$  in certain hydrogen containing solvents noteably water. For example  $NH_3$  and  $CH_3OH$  are highly soluble in  $H_2O$  because their molecules can associate with  $H_2O$  (solvent) molecules through H-bonds as shown below :



In addition, compounds containing oxygen such as sulphates freely dissolve in water through H-bond formation.

**D. High viscosity, high heat of vaporisation and high dielectric constant.** Glycerol ( $CH_2OH-CHOH-CH_2OH$ ) is far more viscous than ethyl alcohol ( $C_2H_5OH$ ) because of the fact that glycerol with three OH groups in its molecule can form many more H-bonds per molecule. This results in greater attraction among the molecules of glycerol and hence its resistance to flow is increased. Thus glycerol is more viscous.

The molecules which are capable of forming associated molecules through Hbonding have naturally high heat of vaporisation and high dielectric constant.

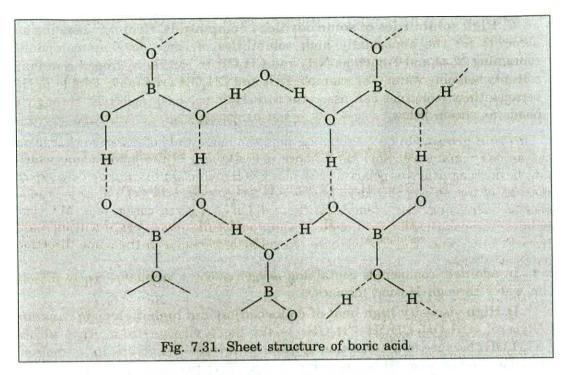
# Significance of Hydrogen Bonding

Apart from providing explanation for a number of abnormal properties of certain compounds containing H-bonding, it is also useful in explaining physiological and geological processess occurring around us. For example :

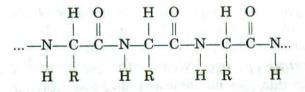
1. Physical state of water. Without H-bonding,  $H_2O$  would have existed as a gas like  $H_2S$ . In that case no life would have been possible without liquid  $H_2O$ .

2. Structure of compounds. H-bonding is directional and on this account it helps in studying and establishing the structure of many compounds like ice, solid hydrogen fluoride, hydrates, solid acids, acid salts etc. For example H-bonding accounts for the tetrahedral structure of ice, zig-zag arrangement of HF molecules in solid hydrogen fluoride and sheet structure of boric acid (Fig. 7.31) which is obtained by joining molecules of boric acid (H<sub>3</sub>BO<sub>3</sub>) by H-bonding, resulting in the formation of infinite parallel sheet.

**3.** Explanation of polymerisation. H-bonding gives a satisfactory explanation for the mechanism of polymerisation and hence of the formation of bigger aggregates of organic as well as inorganic molecules.



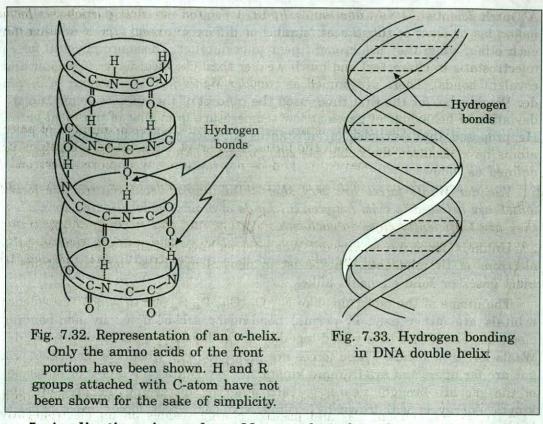
4. Applications in biological investigations. H-bonding also exists in molecules of living systems proteins like various tissues, organs, blood, skin and bones in animals. Fibrous like those found in hair, silk and muscles consist of long chains of a large number (sometimes 1000 or so) of amino acids as shown below. Here R = methyl isopropyl or butyl group.



The long chains of amino acids are coiled about one another into a spiral celled *helix*. Such a helix may be either right-handed (called  $\alpha$ -helix) or left-handed (celled  $\beta$ -helix) as in the case screws.

It has been found that  $\alpha$ -helix constitutes the more stable arrangement. N-H and C=O groups which are vertically adjacent to one another in the helix are linked together by H-bonds. The H-bonds link one spiral to the other (Fig. 7.32). X-ray studies have shown that on an average there are 2.7 amino acid units for each turn of the helix (coil).

Similarly *deoxy ribonucleic acid* (DNA) has two spiral chains which are coiled about each other on a common axis to form a double helix, 18–20 Å in diameter. They are linked together by H- bonding between their sub-units. (Fig. 7.33).



5. Applications in geology. Many geological products such as organic compounds contained in petroleum, coal products and complex hydrates of minerals are formed and established by means of H-bonding.

**6.** In paints and dyes. The adhesive action (i.e. stickness) of glue, honey, dyes and paints is also due to the presence of H-bonding in them.

7. In clothing. H-bond is of vital importance for our clothing. For example the rigidity and tensile strength of cotton, silk or synthetic fibres is due to the H-bonding in them.

8. Food materials. Molecules of most of our food materials like sugars, carbohydrates etc. also consist of H-bonding. For example O-atom of one – OH group of one molecule of sugar and carbohydrate is bonded with –OH group of another molecule through H-bonding.

9. Wood fibres. H-bonding also plays a significant role in making wood fibres more rigid so that they may be used to meet the requirements of housing, furnitures etc.

# van der Waals Forces : Intermolecular Forces

# What are van der Waals Forces?

Till now we had been dealing with the forces or bonds between atoms leading to the formation of molecules. These are called *inter-atomic* or *chemical forces*. A Dutch scientist, J van der Waals in 1873 pointed out that particles (atoms, molecules or ions) of substances (similar or different) exert attractive forces on each other, when they are brought near to each other. These are physical forces (electrostatic in character) and much weaker than chemical forces (*i.e.* ionic and covalent bonds). These are named as *van der Waals forces* in honour of J. van der Waals who, for the first time, used the concept of these forces to explain the deviation of behaviour of gases at low temperature from that of the ideal gases. He proposed that particles of substances interact even if outer-shells of the atoms have acquired the noble gas configurations. Van der Waals forces can be defined as follows :

Van der Waals forces are very short-lived inter-molecular attractive forces which are believed to exist between all kinds of atoms, molecules and ions when they are sufficiently close to each other.

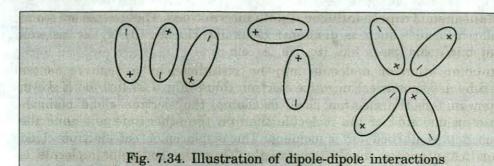
Unlike valence forces, van der Waals forces have nothing to do with valence electrons of the elements. They exist in neutral molecules, ions and atoms of inert gases or solid elements alike.

The atoms of the molecules like  $N_2$ ,  $O_2$ ,  $Cl_2$ ,  $P_4$ ,  $S_8$  etc. in which the valence orbitals are either used in normal bonding or are occupied by non-bonding electrons, are rather firmly held together in the liquid or solid states by van der Waals forces or bonds. These forces are almost absent when the molecules of a gas are far apart and are in rapid kinetic motion. But as the atoms or molecules of the gas are brought nearer to each other by increasing the pressure and kinetic energy is withdrawn by cooling, van der Waals forces are capable of holding the molecules together to form the liquid or solid state. Thus a gas can be liquified by allowing it to expand suddenly from high pressure. During expansion the gas does work in overcoming intermolecular forces of attraction. The energy required for this purpose is obtained from the gas itself, thereby lowering the temperature and causing the liquifaction.

# **Types of van der Waals Forces**

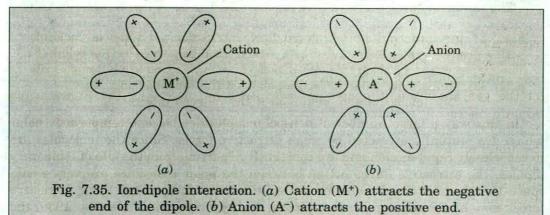
There are four types of van der Waals forces. The origin of each one of these has been explained by a different scientist. The name of scientist has been associated with that type to commemorate his contribution. The four types are :

1. Dipole-dipole interactions. These forces are found in polar molecules having permanent polarity in them. We know that a polar molecule has separate centres of positive and negative charge and possess permanent dipole moment. When polar molecules are brought nearer to each other, they orient themselves in such a way that the positive end of one dipole (polar molecule) attracts the negative end of another dipole and *vice-versa* as shown in Fig. 7.34. Due to this dipole-dipole interaction many molecules are held together. Dipole-dipole interactions between polar molecules are also called *Keesom Forces* and are the strongest of all other types of van der Waals forces. The intensity of these forces is generally hampered by an increase in temperature.

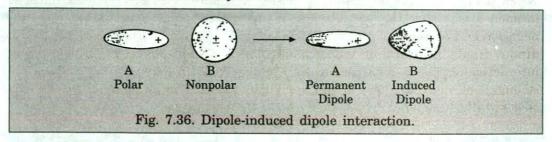


2. Ion-dipole interactions. Polar molecules are attracted towards ions. The negative end of dipoles is attracted towards the cation while the positive end towards the anion (Fig. 7.35).

This type of interaction is called *ion-dipole interaction*. Ion- dipole interactions have been used to explain the dissolution of NaCl in  $H_2O$ . When NaCl is put in  $H_2O$ , it dissolves in it since the negative ends of water molecule dipoles aggregate around Na<sup>+</sup> ions and the positive ends around Cl<sup>-</sup> ions.



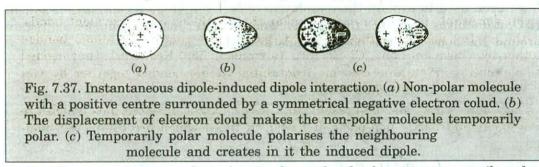
**3. Dipole-induced dipole interactions.** This type of force is found in a mixture containing polar and non polar molecules. When a non-polar molecule is brought near to a polar molecule, the positive end of the polar molecule attracts the mobile electrons of non-polar molecule and thus polarity is induced in non-polar molecule as shown in Fig. 7.36. Now both the molecules become dipoles and hence the positive end of the polar molecule attracts the displaced electron cloud of non-polar molecule. Thus the two types of molecules are held together by forces which are also called *Debye Forces*.



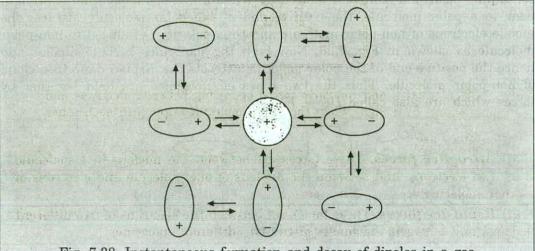
4. Instantaneous dipole-induced dipole interactions. These forces are found in non-polar molecules such as di-atomic gases like  $H_2$ ,  $O_2$ ,  $Cl_2$   $N_2$  etc. as well as mono-atomic noble gases like He, Ne, Ar etc.

A non-polar atom or molecule may be visualised as a positive centre surrounded by asymmetrical negative electron colud [Fig. 7.37 (a)]. Both are in equilibrium. But as the electron cloud oscillates, the electron cloud becomes more dense on one side of the molecule than on the other side and thus the equilibrium gets disturbed for a moment. The displacement of electron cloud creates an instantaneous dipole temporarily. Thus the non-polar molecule is momentarily self-polarised and becomes temporarily polar [Fig. 7.37. (b)].

Now when the self-polarised (*i.e.* temporarily polar) molecule is brought near to a non-polar molecule, it polarises the neighbouring molecule by disturbing its electronic distribution and an induced dipole is created in it, *i.e.* the non-polar molecule momentarily becomes polar [Fig. 7.37 (c)].



In this way a large number of non-polar molecules become temporarily polar which are mutually attracted by weak attractive forces. Since the molecules are in ceaselessly rapid motion and are constantly departing from the site of temporary dipoles, the attractive forces acting between the polar molecules are very weak. Since the electron cloud densities are continuously fluctuating, these attractive forces may be formed and broken quickly. According to Frintz London (1930) the instantaneous formation and subsequent decay of dipoles in a gas due to temporary distortion of electron cloud may be depicted as in Fig. 7.38.



The weak inter molecular forces operating in gases due to instantaneous polarisation of non-polar molecule are also called *London Forces*. These forces are very weak and are known to operate in all types of molecules. These forces are weaker in most cases than dipole-dipole or ion-dipole forces, but are responsible for bringing about condensation of gases, even of noble gases. These forces become stronger with the increase of number of electrons in molecules/ atoms. The forces become stronger with the increase in boiling points of the molecules as shown below :

Molecules / Atoms	:	He	$H_2$	Ne	$N_2$	$O_2$	Ar	$F_2$
No. of electrons	:	2	2	10	14	16	18	18
Boiling points (°C)	:	-269	-253	-246	-196	-183	-186	-186
Strength of London forces	:	15175	S	trengti	h incre	easing	10112 11	

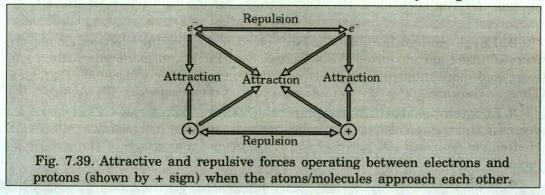
# Nature of van der Waals Forces

van der Waals forces are much weaker than both ionic and covalent bonds, e.g. the energy needed to dissociate a  $Cl_2$  molecule (containing atoms bonded together by a covalent bond, Cl–Cl) into its atoms is 58.0 Kcal while that needed for sublimating crystalline chlorine (containing atoms bonded together by van der Waals forces) is only 6.02 Kcal.

These forces may also be present, to a lesser extent, in molecules which are partly polar and partly non-polar and even in those which are completely nonpolar.

## **Origin of van der Waals Forces**

When two atoms or molecules approach each other, both attractive and repulsive forces operate between their negative electrons and positive protons (nucleus) as shown in Fig. 7.39. Protons have been shown by + sign.



#### These forces are :

(i) Attractive forces. These forces act between the nucleus of a molecule and its own electrons, and between the nucleus of one molecule and electrons of the other molecule.

(ii) **Repulsive forces.** These forces act between the electrons of two different molecules, and between the nuclei of the two different molecules.

The attractive and repulsive forces are in equilibrium at an inter-molecular distance which is, approximately equal to  $4 \text{ Å} (1 \text{ Å} = 10^{-10} \text{ m})$ . However, at intermolecular distance between 4 Å to 10 Å, attractive forces predominate. It is these attractive forces which are acting between the molecules and are called van der Waals forces.

# Factors Affecting the Strength and Magnitude of van der Waals Forces

Following are the important factors that determine the strength and magnitude of van der Waals forces.

**1. Large number of electrons in molecules.** With the increase in the number of electrons in a molecule, the magnitude of van der Waals forces between the molecules also increases. On account of larger number of electrons in a molecule, there is a greater diffusion of electron clouds. This results in a greater polarisation and hence inter-molecular interactions (*i.e.* van der Waals forces) also increase. Since the molecular weight is roughly proportional to the number of electrons in the molecular weight. The boiling point or melting point of a substance is taken as a measure of the magnitude of van der Waals forces.

With the increase of van der Waals forces the boiling point or melting point of a substance also increases. For inert gases the relationship between the number of electrons, molecular weight and boiling point, and magnitude of van der Waals forces is shown below :

Inert gases	:	He	Ne	Ar	Kr	Xe	Rn
No. of electrons	:	2	10	18	36	54	86
Mol. wt.	:	4	20	40	83.7	131	222
Boiling point (°C)	:	-269	-246	-186	-152	-107	-62
Magnitude of van der Waals forces	;	<u></u>	and a second	— Incre	asing —	4, <sup>11</sup> 2	$\longrightarrow$

2. Large molecular size. In large-sized molecules the electron clouds are more diffused and distorted. This brings about more and more polarisation and more and more inter-molecular attraction, hence stronger van der Waals forces. Thus, larger molecules are held together by stronger van der Waals forces.

**3. Low temperature.** At low temperature, the random movements of molecules decrease and they come closer to each other and thus they interact more effectively. Hence, *low temperature increases the strength and magnitude of van der Waals forces.* 

4. High pressure. At high pressures the molecules come closer and it results into strong inter-molecular interactions or van der Waals forces. Thus, *higher* the pressure, stronger will be the van der Waals forces.

# **Applications of van der Waals Forces**

Although van der Waals forces are weak, yet they have been used to explain many important phenomena. For example :

- (i) It is the van der Waals forces between the molecules that cause substances like inert gases, halogens etc. to condense to liquids and to freeze into solids, when the temperature is considerably lowered. Thus these forces are responsible for bringing about condensation and crystallisation (at low temperatures) in the noble gases and halogens.
- (ii) These forces account for varied hardness of certain solids. If the atoms or molecules in any crystal are united only by van der Waals forces, the crystals can be broken down easily. Such crystals will be soft and possess low melting points.
- (*iii*) These forces, though extremely weak, can explain the deviation of the behaviour of gases at low temperature from that of the ideal gases. The details of this application may be found in the chapter on *Kinetic Theory* of Gases which may be studied from some *Physical Chemistry Book*.

# **Questions with Answers**

Q.1 Arrange the following compounds in the order of their increasing melting points :

(i) LiF, LiCl, LiBr, LiI (ii) LiCl, NaCl, KCl, RbCl, CsCl.

**Ans :** The answer to this question can be given either on the basis of Fajans'rules or on the basis of the relation between the electronegativity diffirence between two concerned atoms and ionic character in the bond between two atoms.

(i) Greater the electronegativity difference between the two concerned atoms, greater would be the ionic character and higher would be the melting point.

LiF > LiCl > LiBr > LiI

(ii) Due to covalent character LiCl has lower melting point.

 $\therefore$  LiCl < NaCl > KCl > RbCl > CsCl.

Bond length (d) - 1590 nm (Given)

Q.2 The ionic character in certain A-B bond is 76.81% and the bond length A-B is 159.0 pm. Calculate dipole moment of AB molecule.

Ans : Ionic character in A-B bond = 76.81% (Given)

$$= 159.0 \times 10^{-10} \text{ cm} \quad (\because 1 \text{ pm} = 10^{-10} \text{ cm})$$

$$= 159.0 \times 10^{-10} \text{ cm} \quad (\because 1 \text{ pm} = 10^{-10} \text{ cm})$$

$$we \text{ know that } q = 4.8 \times 10^{-10} \text{ esu}$$

$$\mu_{exp} = ?$$

$$\mu_{cal} = q \times d = (4.8 \times 10^{-10} \text{ esu}) \times (159 \times 10^{-10} \text{ cm})$$

$$= 4.8 \times 159 \times 10^{-20} \text{ esu.cm}$$

$$\% \text{ ionic character} = \frac{\mu_{exp}}{\mu_{cal}} \times 100$$

$$\text{or } 76.81 = \frac{\mu_{exp} \times 100}{4.8 \times 159 \times 10^{-20} \text{ esu.cm}}$$

$$\therefore \qquad \mu_{exp} = \frac{76.81 \times 4.8 \times 159 \times 10^{-20}}{100} \text{ esu.cm}$$

Modern Inorganic Chemistry

$$= \frac{76.81 \times 4.8 \times 159 \times 10^{-2}}{10^2} \times 10^{-18} \text{esu.cm}$$
  
= 76.81 × 4.8 × 159 × 10<sup>-4</sup>D (:: 10<sup>-18</sup> esu.cm = 1D)  
= 58621.392 × 10<sup>-4</sup>D  
= **5.86 D (Ans)**

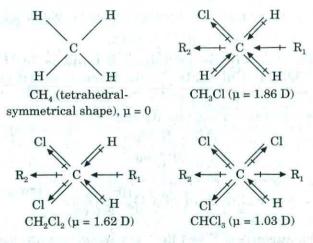
Q.3 The observed value of dipole moment of  $H_2O$  molecule is found to be 1.84 D. Calculate the H–O–H bond angle in  $H_2O$  molecule, given that the bond moment of O–H bond is 1.5 D.

Ans : 
$$\mu_{H_2O} = 1.84$$
 D (Given)  
 $\mu_{OH} = 1.5$  D (Given)  
If H-O-H bond angle is ∞, then we have :  
 $\mu^2_{H_2O} = \mu^2_{OH} + \mu^2_{OH} + 2 \times \mu_{OH} \times \mu_{OH} \times \cos \infty$   
 $= (1.5)^2 + (1.5)^2 + 2 \times 1.5 \times 1.5 \times \cos \infty$   
 $= 2.25 + 2.25 + 4.5 \times \cos \infty$   
or  $(1.84)^2 = 4.5 + 4.5 \cos \infty$   
 $\therefore \cos \infty = \frac{(1.84)^2 - 4.5}{4.5} = \frac{3.3856 - 4.5}{4.5}$   
or  $\cos \infty = -0.2476$ 

 $\infty = 104^{\circ} 28'$  (Ans)

Q.4 Arrange the following molecules in the decreasing order of their dipole moment :  $CH_4$ ,  $CH_3Cl$ ,  $CH_2Cl_2$  (cis form) and  $CHCl_3$ .

Ans : The structures of the given molecules are given below. The direction of bond moment has also been shown



 $CH_4$  molecule ( $\mu = 0$ ) This molecule has tetrahedral shape (symmetrical shape). Hence  $\mu$  for this molecule = 0

CH<sub>3</sub>Cl molecule ( $\mu = 1.86$  D). In this molecule, the resiltant (R<sub>1</sub>) of two C-H bond moments adds to the resultant (R<sub>2</sub>) of C-H and C-Cl bond moments.

or

 $CH_2Cl_2$  molecule ( $\mu = 1.62$  D). In this molecule, the resultant ( $R_1$ ) of two C-H bond moments adds to the resultant ( $R_2$ ) of two C-Cl bond moments.

**CHCl<sub>3</sub> molecule** ( $\mu = 1.03$  D). In this molecule the resiltant ( $R_1$ ) of C-H and C-Cl bond moments oppose the resultant ( $R_2$ ) of two C-Cl bond moments.

In CH<sub>3</sub>Cl and CH<sub>2</sub>Cl<sub>2</sub> molecules, the resultants  $R_1$  and  $R_2$  are equal but  $R_2$ in CH<sub>3</sub>Cl is more than  $R_2$  in CH<sub>2</sub>Cl<sub>2</sub>. Hence the sum,  $(R_1 + R_2)$  for CH<sub>3</sub>Cl is greater than the sum,  $(R_1 + R_2)$  for CH<sub>2</sub>Cl<sub>2</sub>. In other words  $\mu$  of CH<sub>3</sub>Cl is greater than that of CH<sub>2</sub>Cl<sub>2</sub>. In CHCl<sub>3</sub>, since  $R_1$  and  $R_2$  oppose each other,  $\mu$  for CHCl<sub>3</sub> is less than CH<sub>3</sub>Cl and CH<sub>2</sub>Cl<sub>2</sub> both.

Above discussion shows that the decreasing order of dipole moments values are :

CH <sub>3</sub> Cl	>	$CH_2Cl_2$	>	CHCl <sub>3</sub> >	CH4
1.86 D		1.62 D		1.03 D	0.0 D

Q.5 Which of the compounds  $viz \operatorname{SnCl}_2$ ,  $\operatorname{SnCl}_4$ ,  $\operatorname{SnF}_2$  and  $\operatorname{SnF}_4$  is the least covalent?

Ans: Out of given halides,  $SnF_2$  is the least covalent. This can be explained as follows with the help of Fajan's rules.

Due to smaller size of  $\operatorname{Sn}^{4+}$  ion as compared to that of  $\operatorname{Sn}^{2+}$  ion,  $\operatorname{SnCl}_4$  is more covalent than  $\operatorname{SnCl}_2(\operatorname{SnCl}_4 > \operatorname{SnCl}_2)$ . Simiarly  $\operatorname{SnF}_4$  is more covalent than  $\operatorname{SnF}_2(\operatorname{SnF}_4 > \operatorname{SnF}_2)$ . Out of  $\operatorname{SnF}_2$  and  $\operatorname{SnCl}_2$ , due to large size of  $\operatorname{Cl}^-$  ion as compared to that of  $F^-$  ion,  $\operatorname{SnCl}_2$  is more covalent than  $\operatorname{SnF}_2$ . Thus  $\operatorname{SnF}_2$  is the least covalent.

Q.6 In each of the following pairs of compounds, which one is more covalent and why?

(i) AgCl, AgI (ii) BeCl<sub>2</sub>, MgCl<sub>2</sub> (iii) SnCl<sub>2</sub>, SnCl<sub>4</sub> (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<sup>-</sup> ion and hence is more polarized than Cl<sup>-</sup> ion.

(*ii*) BeCl<sub>2</sub> is more covalent than MgCl<sub>2</sub>. This is because Be<sup>2+</sup> ion is smaller in size than Mg<sup>2+</sup> 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.7 BeCO<sub>3</sub> is less stable than MgCO<sub>3</sub>. Explain.

Ans: Lower stability of  $BeCO_3$  as compared to that of  $MgCO_3$  can be explained on the basis of Fajan's rules. Since  $Be^{2+}$  ion is smaller in size than  $Mg^{2+}$  ion,  $BeCO_3$  is covalent (lesser ionic) while  $MgCO_3$  is ionic. Being covalent,  $BeCO_3$  is less stable than  $MgCO_3$  which is ionic. It in due to lesser stability of  $BeCO_3$  that it gets decomposed into BeO and  $CO_2$  on heating

 $BeCO_3 \xrightarrow{\Delta} BeO + CO_2$ 

Q.8 How many H-bonds are formed by each  $H_2O$  molecule in the structure of liquid water and how many water molecules are attached to each  $H_2O$  molecule and in what direction ?

Ans : If we examine the structure of liquid water, we find that :

(i) Each  $H_2O$  molecule forms four H-bonds : two H-bonds are formed by O-atom of  $H_2O$  molecule and two H-bonds are formed by two H-atoms of the same  $H_2O$  molecule.

(*ii*) Each  $H_2O$  molecule is linked **tetrahedrally** with four  $H_2O$  molecules through H-bonds.

Q.9 Discuss the structuer of ice.

or Explain why ice has lower density than water.

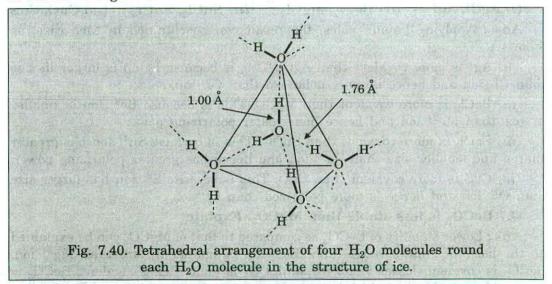
or Explain why ice floats on water.

or Explain why ice is lighter than water.

**Ans**: When liquid water is allowed to freez, it is converted into solid, called ice. Thus ice is the solid form of liquid water. Ice has larger volume than liquid water.

Liquid water –	Freezing	$\rightarrow$ Solid water (Ice)
Liquid water -		
(Less volume)		(Larger volume)

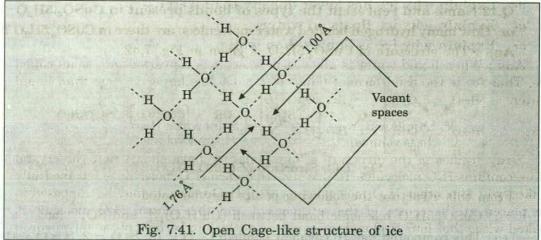
X-ray studies of the structure of hexagonal ice have shown that the crystal of ice contains  $H_2O$  molecules. In this structure each  $H_2O$  molecule is tetrahedrally linked will four other  $H_2O$  molecules, *i.e.* one  $H_2O$  molecule may be supposed to be placed at the centre of the tetrahedron and this central  $H_2O$  molecule is linked with other four  $H_2O$  molecules placed at the four corners of the tetrahedron as shown in Fig. 7.40.



It may be seen from Fig. 7.40. that each O-atom of each  $H_2O$  molecule is linked with four H-atoms. O-atom is linked with two H-atoms of its own  $H_2O$ molecule by strong covalent bonds (shown by solid lines) and with two H-atoms of the neighbouring two  $H_2O$  molecules by two H-bonds (shown by dotted lines).

This structure shows that O-atom of each  $H_2O$  molecule can form maximum two H-bonds with other two  $H_2O$  molecules and each H-atom of each  $H_2O$  molecule can form only one H-bond with O-atom of the neighbouring  $H_2O$  molecule. Thus each  $H_2O$  molecule, as a whole, can form maximum four H-bonds with other four  $H_2O$  molecules, *i.e.* each  $H_2O$  molecule is linked tetrahedrally with four  $H_2O$ molecules by H-bonds.

Since O...H hydrogen bonds are longer (= 1.76 Å) than O-H covalent bonds (= 1.00 Å),  $H_2O$  molecules in the crystal structure of ice are not closely packed together and hence there exist a number of vacant spaces between  $H_2O$  molecules. The presence of vacant spaces gives **open cage-like structure** to ice (see Fig. 7.41).



Due to the presence of vacant spaces in the structure of ice, ice has relatively larger volume than the liquid water of the same mass and hence density of ice is lower than that of liquid water. It is due to lower density of ice that it (*i.e.* ice) floats on water. When we say that ice has lower density than water, this means that ice is lighter than water.

# Q.10 Find out the number of bonds formed by O-atom of each H<sub>2</sub>O molecule in ice.

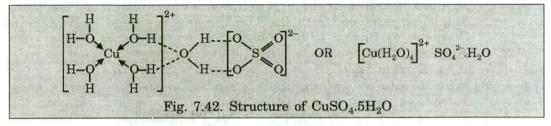
Ans: If we examine the structure of ice, we find that O-atom of each  $H_2O$  molecule is linked with its two H-atoms by two O - H covalent bonds and with two H-atoms of other two  $H_2O$  molecules by two O...H hydrogen bonds. Thus total number of bonds formed by O-atom is 4.

# Q.11 Discuss the action of heat on ice.

# or Explain that water has maximum density at 4° C.

Ans: We know that ice has open cage-link structure which contains a number of  $H_2O$  molecules which are linked with one another by H-bonds. This structure also contains vacant spaces between  $H_2O$  molecules. When ice is heated, it melts and is converted into liquid water. During melting H-bonds existing between different  $H_2O$  molecules in the open cage-link structure of ice start breaking and water molecules are separted from ice. These separated water molecules occupy vacant spaces exiting in the open-cage structure of ice. This results in that water molecules come closer to each other and hence volume decreases. With the decrease in volume, the density of liquid water increases. The increase in density of water takes place only in the temperatuer range 0°C to 4°C. After 4°C, the kinetic energy of water molecules increase and hence they once again start moving away from each other. This causes expansion in volume of liquid water. Thus the volume of liquid water increases. The increases in volume decreases the density of liquid water. Thus above 4°C the density of water starts decreasing. The above discussion shows that when ice is melted, it is converted into liquid water. The density of liquid water increases upto 4°C but beyond 4°C the density starts decreasing.Thus water has maximum density at 4°C.

Q.12 Name and represent the types of bonds present in  $CuSO_4.5H_2O$ or How many hydrogen-bonded water molecule(s) are there in  $CuSO_4.5H_2O$ ? Ans : The structure of  $CuSO_4.5H_2O$  is given in Fig. 7.42.



From this structure the following points may be noted :

(i)  $CuSO_4.5H_2O$  has ionic bond between  $[Cu(H_2O)_4]^{2+}$  and  $SO_4^{2-}$  ions,

(ii) This compound has 16 covalent bonds  $(O - H = 10, S - \overline{O} = 2, S = O = 4)$ .

(*iii*) Four  $H_2O$  molecules are linked with  $Cu^{2+}$  ion in coordination sphere by 4 coordinate bonds. Thus  $CuSO_4.5H_2O$  has four coordinate bonds ( $H_2O \rightarrow Cu^{2+}$ ).

(iv) The remaining H<sub>2</sub>O molecule forms four H-bonds. Two H-bonds are formed by two H-atoms with two O-atoms of  $SO_4^{2-}$  ion and two H-bonds are formed by O-atom with H-atoms of two coordinated H<sub>2</sub>O molecules present in coordination sphere.

Q.13 Explain the mechanism for the formation of  $KHF_2$  by the combination of KF and HF in aqueous solution.

or KF combines with HF to form KHF<sub>2</sub> but KCl, KBr and KI donot combine with HCl, HBr and HI to form KHCl<sub>2</sub>, KHBr<sub>2</sub> and KHI<sub>2</sub> respectively. Explain why?

or KHF<sub>2</sub> exists but KHCl<sub>2</sub>, KHBr<sub>2</sub> and KHI<sub>2</sub> do not exist. Explain why?

or  $KHF_2$  contains K<sup>+</sup> and  $HF_2^-$  ions but does not contain K<sup>+</sup>, H<sup>+</sup> and  $2F^-$  ions. Explain.

Ans : When KF combines with HF in aqueous solution, KHF<sub>2</sub> is formed.

 $KF \rightarrow K^+ + F^-$ 

$$F^- + HF \rightarrow F^- \dots H - F$$
 or  $[HF_2]^-$ 

On adding : KF + HF  $\rightarrow$  K<sup>+</sup> [HF<sub>2</sub>]<sup>-</sup>

The formation of  $HF_2^-$  ion takes place due to the attachment of  $F^-$  ion to H-atom of HF molecule through H-bonding. Due to smaller electronegative of CI-, Br- and I- these ions cannot combine with HCl, HBr and HI to form [HCl\_]-, [HBr2] and [HI2] ions respectively. Due to non-formation of these ions, K[HCl2], K [HBr2] and K [HI2] donot exits. In other words we can say that KCl, KBr and KI cannot combine with HCl, HBr and HI and cannot form K [HCl2], K [HBr2] and K [HI2] respectively. Above discussion shows KHF2 contains K+ and [HF2]and not K<sup>+</sup>, H<sup>+</sup> and F<sup>-</sup> ions.

# **University Questions**

- 1. Discuss any two rules proposed by Fajan. (Himachal Pradesh 2000)
- 2. (a) What is inert pair effect? List the elements of p-block for which inert pair effect is predominant.
  - (b) Explain (i) Boron forms no compounds in unipositive oxidation but thallium in unipositive state is quite stable. (ii) Al forms the ion,  $[AIF_6]^{3-}$ but boron does not form the ion, [BF<sub>6</sub>]<sup>3-</sup>. (iii) Bond angle in oxides decreases as  $Br_2O > Cl_2O > OF_2$ . (Himachal Pradesh 2000)
- 3. (a) Nitrogen forms only  $NCl_3$  but phosphorus forms both  $PCl_3$  as well as PCl<sub>5</sub>. Explain why?
  - (b) Write a note on (i) Sidgwick's maximum covalency rule. (ii) Variable valency. (Kanpur 2000)
- 4. (a) Write a note on "Free electron theory of metallic bonding".

(b) Give an account of odd electron bond. (Kumaon 2000)

5. (a) Explain the following :

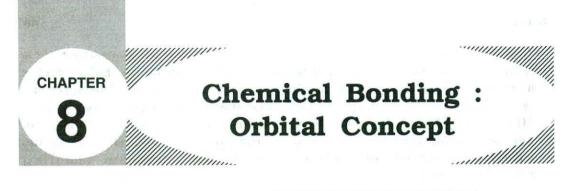
(i) NaCl is soluble in water but not in chloroform.

(ii) Though ethanol is a covalent compound it is soluble in water.

- (b) Write a note on "Resonance". [Gauhati (General) 2001] 6. Explain the following :
  - (i)  $NCl_5$  is not formed while  $PCl_5$  is formed.
  - (ii) Bond angle of PH<sub>3</sub> is less than NH<sub>3</sub>.
  - (iii) Al forms  $[AIF_6]^{3-}$  ion but boron does not form  $[BF_6]^{-3}$ .
  - (iv) NH<sub>3</sub> has a dipole moment but BF<sub>3</sub> is non polar. (Lucknow 2000)
- 7. (i) Explain the following :
  - (a)  $AlF_3$  is ionic while  $AlCl_3$  is covalent.
  - (b) AgI is covalent whereas Nails ionic.
  - (c) Phosphorus forms PCl<sub>3</sub> and PCl<sub>5</sub> both while nitrogen forms only NCl<sub>3</sub>.
  - (ii) Write short note on : (a) Diagonal relationship (b) inert pair effect (c) Hydrogen bond (d) Electropositivity. (Avadh 2000)
- (i) Explain why LiCl is insoluble in water. 8.
  - (ii) Write a note on "Inert pair effect". (Lucknow 2001)
  - (*iii*) Explain  $\sigma$  and  $\pi$  bonds.
- 9. Which of the following compounds does not contain ionic bond ? NaOH, K<sub>2</sub>S, HCl and LiH. (H.N. Bahuguna 2006)
- 10. Which of the following is the most covalent ? BeCl<sub>2</sub>, MgCl<sub>2</sub>, CaCl<sub>2</sub> and SrCl<sub>2</sub>. (Agra 2008)
- 11. (i) Write a note an Fajans rules (ii) Explain intermolecular H-bonding
- **12.** Cu<sub>2</sub>Cl<sub>2</sub> is more covalent than NaCl. Why ?

(Meerut 2009)

(Meerut 2008)



# Linnett's Double-Quartet (D-Q) Theory

The octet theory given by Lewis and Langmuir has been found unsuccessful in explaining the paramagnetic behaviour of some molecules.

In 1961 Linnett modified octet theory and gave a satisfactory explanation of the paramagnetism of the molecules. According to Linnett's D-Q theory, eight valence-shell electrons (*i.e.* an octet) of an atom can be considered to be made up of two groups of four electrons instead of a group of four localised pairs of electrons. One group has 4 electrons of one spin while the other group also has 4 electrons of the other spin. Thus according to Linnett, the octet of valence shell electrons is treated as a *double-quartet* (D-Q) of electrons. The distribution of electrons round a given nucleus is governed by two factors.

**1.** Spin correlation. It is because of spin correlation that the electrons of the like spin tend to keep apart and those of unlike spin tend to come together (*Pauli's exclusion principle*).

2. Charge correlation. This arises because of the repulsion between the particles of like charge and it also keeps the electrons of the like spin apart.

Thus we see that for paired electrons the spin correlation is opposed to the charge correlation. In order to make the inter-electronic repulsion minimum four electrons of each quartet set tend to arrange themselves at the vertices of two inter-connected tetrahedra. The state of minimum inter-electronic repulsion is achieved when the vertices of one tetrahedron lie at the centre of the faces of the other tetrahedron (Fig. 8.1).

# To Explain the Magnetic Behaviour of $O_2$ and $N_2$ Molecules on the Basis of D-Q Theory

Now let us take the examples of  $O_2$  and  $N_2$ molecules to illustrate the use of Linnett's D-Q theory in explaining their structure and magnetic behaviour.

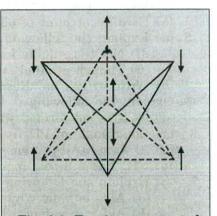
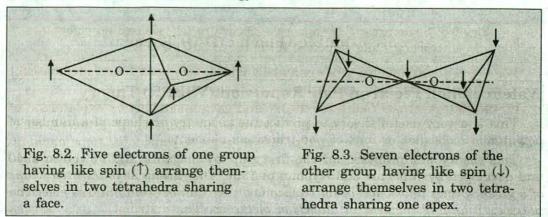


Fig. 8.1. Two inter-connected tetrahedra having two sets of 4 electrons. Four electrons of one set having like spin have been shown as  $\uparrow$  while the four electrons of the other set have been shown as  $\downarrow$ . The vertices of one tetrahedron lie at the centre of the faces of the other tetrahedron. This arrangement gives minimum inter-electronic repulsion.

#### Chemical Bonding (Orbital Concept)

1.  $O_2$  molecule. On the basis of D-Q theory, 12 valence- shell electrons of  $O_2$  molecule can be considered to be made up of two groups—one group has 5 electrons of one spin while the other group has 7 electrons of the other spin. Five electrons of one group having like spin arrange themselves in two tetrahedra sharing a face (Fig. 8.2) while the seven electrons of the other group having like spin arrange themselves in two tetrahedra sharing a face (Fig. 8.2) while the seven electrons of the other group having like spin arrange themselves in two tetrahedra sharing one apex (Fig 8.3). Both the arrangements have minimum energy.

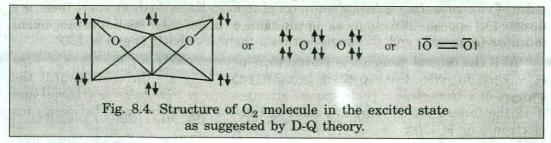


On superimposing the two arrangements shown in Fig. 8.2 and 8.3, we obtain the structure of  $O_2$  molecule in the ground state as :

$$\begin{array}{c} \downarrow \uparrow O \uparrow \downarrow O \uparrow \downarrow O \downarrow \downarrow \end{array}$$

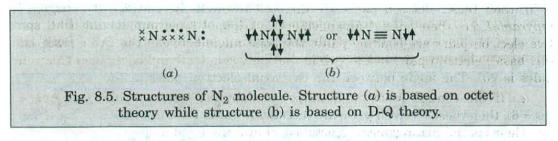
In the above structure 5 electrons of one set have been shown as  $\uparrow$  while 7 electrons of the other set have been shown as  $\downarrow$ . — represents an electron pair of opposite spins. This structure of  $O_2$  molecule in its ground state satisfies all the requirements *viz.* 2 unpaired electrons (*paramagnetic behaviour*), 8 electrons around each O-atom and 4 electrons in the inter-nuclear region.

Twelve electrons of  $O_2$  molecule in the excited state (159 KJ. mole<sup>-1</sup> above the ground state) can be consider to be made up of two sets of 6 electrons which are arranged as 6 pairs at the corners of two tetrahedra sharing one edge between them (Fig. 8.4). This structure does not contain any unpaired electrons and hence well explains the diamagnetic nature of  $O_2$  molecule in the excited state.



2.  $N_2$  molecule. According to D-Q theory 10 valence-shell electrons of  $N_2$  molecule are made up of two sets each of which has 5 electrons of the same spin

(See Fig. 8.5). Thus we find that both octet theory and D-Q theory suggest that  $N_2$  molecule has bond order of three (six electrons between the nuclei) and is *diamagnetic* because of spin cancellation.



# Valence Shell Electron Pair Repulsion (VSEPR) Theory

This is a very useful theory to predict the geometry or shape of a number of polyatomic molecules or ions of non-transition elements.

This theory was proposed for the first time by Sidgwick and Powell in 1940 and developed by Gillespie and Nyholm in 1957. This theory says that the shape of a given species (molecule -or ion) depends on the number and nature of electron pairs surrounding the central atom/ion of the species.

This theory makes the following assumptions :

# Assumptions of VSEPR Theory

1. Spatial arrangement of electron pairs round the central atom/ion of a given molecule/ion. The electrons already present in the valence-shell of the central atom/ion of a given species (= a) plus the electrons acquired by the central atom/ion as a result of bonding with other atoms (= b) are called its *valence-shell* electrons. Half of (a + b), *i.e.* (a + b)/2, gives the number of electron pairs present in the valence-shell of the central atom/ion. This theory assumes that these electron pairs occupy localised orbitals which arrange themselves in space in such a way that they keep apart from one another as far as possible so that they may experience minimum electrostatic repulsion between them and hence may give minimum energy and maximum stability to the species.

According to this assumption :

(a) If the central atom/ion is surrounded by two electron pairs, *i.e.* if the sum of bonding electron pairs (bps) and non-bonding electron pairs, also called lone pairs of electrons (lps) is two, then in order to keep them farthest apart these are directed in opposite directions along the same axis, *i.e.* their spatial arrangement is *linear* (*diagonal*) and the angle between them (*i.e.* bond angle) is 180°.

(b) If the central atom/ion is surrounded by three electron pairs (*i.e.* bps + lps = 3), then in order to keep them farthest apart they are directed towards the corners of a *triangle*, *i.e.* their spatial arrangement is *triangular* or *trigonal* and if all the three electron pairs are bonding electron pairs, the angle between each electron pair is  $120^{\circ}$ .

(c) If the central atom/ion is surrounded by four electron pairs (*i.e.* bps + lps = 4), then these electron pairs are directed towards the corners of a regular

#### Chemical Bonding (Orbital Concept)

tetrahedron i.e. their spatial arrangement is tetrahedral and if all the four electron pairs are bps, the bond angle is  $109.5^{\circ}$ .

(d) If the central atom/ion is surrounded by *five* electron pairs (*i.e.* bps + lps = 5), then these electron pairs are directed towards the corners of a *trigonal* bipyramid, *i.e.* their spatial arrangement is trigonal bipyramidal and if all the five electron pairs are bonding pairs, the bond angle between the two equatorial (*i.e.* basal) electron pairs is 120° while that between axial and equatorial electron pairs is 90°. The angle between the two axial electron pairs is 180°.

(e) If the central atom/ion is surrounded by six electron pairs (*i.e.* bps + lps = 6), then these electron pairs are directed towards the corners of a octahedron, *i.e.*, their spatial arrangement is octahedral and the bond angle between the two adjacent (*cis*) electron pairs is 90° while the angle between the axial (*trans*) electron pairs is 180°.

(f) If the central atom/ion is surrounded, by seven electron pairs (*i.e.* bps + lps = 7), then these electron pairs are directed towards the corners of a pentragonal bipyramid and hence their spatial arrangement is pentagonal bipyramidal. The angle between the two equatorial electron pairs is 72° while that between the equatorial and axial electron pairs is 90°. The angle between the two axial electron pairs is 180°.

Relationship between the number of electron pairs (*i.e.* bps + lps) round the central atom/ion of a given species, the spatial arrangement of the electron pairs and the bond angle (provided that all the electron pairs are bonding electron pairs. *i.e.* there are no lone pairs of electrons) is shown as follows :

	No. of electron pairs (bps + lps)		2	3	4	5	6	
	Spatial arrange- ment of electron pairs round the central atom/ion	ſ	Linear	Trigonal planar		Trigonal bipyra- midal		Pentagonal biyramidal
7	Bond angles provided that all the electron pairs are bps	}: }	180°	120°	109.5	120°, 90°	90°	72°, 90°

2. Regular and irregular geometry of the molecule/Ion. The electron pairs surrounding the central atom/ion are either bps or some of them are bps and the remaining are lps. If the central atom/ion is surrounded only by the bps, then the species has a regular geometry, i.e. there is no distortion in the shape of the species. If, however, the central atom/ion is surrounded by the bps as well as by lps, the bond angle gets altered from the value expected for a particular geometry of the molecule or ion. Now since the magnitude of bond angle gives an idea of the geometry of the molecule or ion, the change in the magnitude of the bond angle also changes the geometry of the molecule or ion, i.e. with the change of the magnitude of the bond angle, the shape of the molecule or ion gets distorted. In short we can say that the presence of one or more lone pairs of electrons on

the central atom changes the magnitude of bond angle which, in turn, changes the geometry of the molecule or ion i.e. the presence of one or more lone pairs of electrons in the valence shell of the central atom or ion gives *irregular* or *distorted* geometry to the molecule or ion.

**Cause of change in bond angle.** The change in the magnitude of bond angle is due to the fact that  $(lp\_lp)$  repulsion is greater than  $(lp\_bp)$  repulsion which, in turn, is greater than  $(bp\_bp)$  repulsion, *i.e.* 

# (lp-lp) repulsion > (lp-bp) repulsion > (bp-bp) repulsion

Here lp and bp have been used to represent the lone pairs and bonding pairs of electrons surrounding the central atom. Since a bp experiences less repulsion from another bp than from a lp, it (*i.e.* bp) becomes closer to the bp and a contraction in the bond angle (*i.e.*, the angle between the two bps) occurs.

More the number of lps on a central atom, the greater is the contraction caused in the angle between the bps. This fact is clear when we compare the bond angles in CH<sub>4</sub>, NH<sub>3</sub> and H<sub>2</sub>O molecules.

Molecules		$CH_4$	$\mathrm{NH}_3$	$H_2O$
No. of lps on the central atom		0	1	2
Bond angle (Angle between two bps)	$\Big\}:$	109.5°	107.5°	$105.5^{\circ}$
Contraction in bond angle relative to that of $CH_4$	}:	0	$109.5^{\circ}-107.5^{\circ}$ = $2^{\circ}$	$109.5^{\circ}$ $-105.5^{\circ} = 4^{\circ}$

The comparison of bond angles of  $NH_3$  and  $H_2O$  with that of  $CH_4$  shows that each of H—O—H bond angles in  $H_2O$  is decreased from a tetrahedral angle (= 109.5°) to a greater extent than each of H—N—H bond angles in  $NH_3$ . The greater decrease in case of  $H_2O$  is explained as follows :

The valence-shell of O-atom in  $H_2O$  molecule has four electron pairs as N-atom in  $NH_3$  molecule has. Two of these electron pairs are *bps* each of which is attracted by two nuclei (of H and O atoms) while the remaining electron pairs are *lps* each of which is attracted only by one nucleus (of O-atom), since these *lps* orginate from O-atom only. Thus we see that O-atom in  $H_2O$  molecule has two *lps* while N-atom in NH<sub>3</sub> molecule has only one *lp* on it. Consequently in  $H_2O$  molecule there are three types of electron pair—electron pair repulsions which are (*i*) (*lp*—*lp*) repulsion (*ii*) (*lp*—*bp*) repulsion and (*iii*) (*bp*—*bp*) repulsion while in NH<sub>3</sub> molecule there are only two types of repulsions which are (*i*) (*lp*—*bp*) repulsion (*ii*) (*bp*—*bp*) repulsion and (*iii*) (*bp*—*bp*) repulsion (*see* Fig. 8.6.).

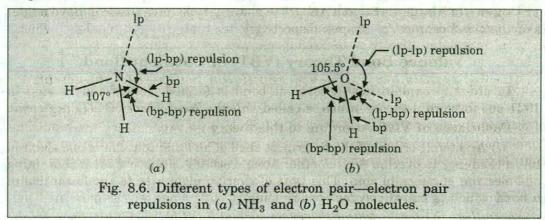
The magnitude of these repulsions, as shows above, is the following order : (lp-lp) repulsion > (lp-bp) repulsion > (bp-bp) repulsion

The net effect of this difference in electron pair—electron pair repulsions is that the two lps on O-atom force the two (O—H) bps to come more closer to each other than one lp on N-atom in NH<sub>3</sub> molecule forces three (N—H) bps to come closer to each other. Thus each of H—O—H bond angles in H<sub>2</sub>O is decreased from a tetrahedral angle to a greater extent than each of H—N—H bond angles in NH<sub>3</sub>

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#### Chemical Bonding (Orbital Concept)

(H—N—H bond angle in  $NH_3 = 107.5^\circ$ , H—O—H bond angle in  $H_2O = 105.5^\circ$ ). Due to the decrease in the expected tetrahedral angle, shape of  $H_2O$  molecule gets distorted and hence  $H_2O$  molecule assumes *planar V-shape* (angular or bent shape).



#### Shape of Molecules/Ions on the basis of VSEPR Theory

**1.** Shape of molecules/ions whose central atom/ion has two electron pairs. Such molecules may be of AB<sub>2</sub> (e.g. BeF<sub>2</sub>) type. These have two  $\sigma$ -bonding electron pairs and no lone pair. (bps = 2, lp = 0) These have *linear shape*. Here A is the central atom/ion and B are the atoms bonded to atom A by  $\sigma$ -bonds only.  $\pi$ -bonds are not present.

2. Shape of molecules/ions whose central atom/ion has three electron pairs. Such species may be of  $AB_3$  (bps = 3, lp = 0) and  $AB_2(lp)$  (bps = 2, lp = 1) type. The species of  $AB_3$  (e.g. BF<sub>3</sub>, GaCl<sub>3</sub>) and  $AB_2$  (lp) [e.g. SnCl<sub>2</sub> (gaseous), PbCl<sub>2</sub>] type have trigonal planar and angular or V-shape respectively. Here lp represents the lone pair of electrons in the valence-shell of the central atom/ion, A.

3. Shape of molecules/ions whose central atom/ion has four electron pairs. Such species may be of  $AB_4$  (bps = 4, lp = 0),  $AB_3(lp)$  (bps = 3, lp = 1),  $AB_2(lp)_2$  (bps = 2, lps = 2) and  $AB(lp)_3$  (bp = 1, lps = 3) type. The species of  $AB_4$  (e.g.  $CH_4$ ,  $PCl_4^+$ ,  $SiCl_4$ ,  $BH_4^-$ ,  $NH_4^+$ ),  $AB_3(lp)$  (e.g.  $NH_3$ ,  $PH_3$ ),  $AB_2(lp)_2$  ( $H_2O$ ,  $ICl_2^+$ ,  $SCl_2$ ) and  $AB(lp)_3$  (e.g. ICl) type have regular tetrahedral, trigonal pyramidal, angular or V-shape and linear shape respectively.

4. Shape of molecules/ions whose central atom/ion has five electron pairs. Such species may be of  $AB_5$  (bps = 5, lp = 0),  $AB_4(lp)$  (bps = 4, lp = 1).  $AB_3(lp)_2$  (bps = 3, lps =) and  $AB_2$  (lp)<sub>3</sub> (bps = 2, lps = 3) type. The species of  $AB_5$  ( $e.g. PF_5$ ,  $PCl_5$  (g),  $AB_4(lp)$  (e g.  $SF_4$ ,  $IF_4^+$ ),  $AB_3$  (lp)<sub>2</sub> ( $e.g. CIF_3 BrF_3$ ),  $AB_2$  (lp)<sub>3</sub> ( $e.g. XeF_2 I_3^-$ ,  $ICl_2^-$ ) type have trigonal bipyramidal, distorted trigonal bipyramidal, T-shape and linear structures respectively. The lone pairs occupy the equatorial positions.

5. Shape of molecules/ions whose central atom/ion has six electrons pairs. Such species may be of  $AB_6$  (bps = 6, lp = 0),  $AB_5(lp)$  (bps = 5, lp = 1) and  $AB_4(lp)_2$  (bps = 4, lps = 2) type. The species of  $AB_6$  (e.g. SF<sub>6</sub>, PCl<sub>6</sub><sup>-</sup>),  $AB_5(lp)$  (e.g. SbX<sub>5</sub><sup>-2</sup>, BrF<sub>5</sub>, IF<sub>5</sub>) and  $AB_4(lp)_2$  (e.g. XeF<sub>4</sub>, ICl<sub>4</sub><sup>-</sup>) type have regular octahedral, square pyramidal and square planar shapes respectively. The lone pairs occupy the axial positions.

6. Shape of molecules/ions whose central atom/ion has seven electron pairs. Such species may be of  $AB_7$  (bps = 7, lp = 0) and  $AB_6(lp)$  (bps = 6, lp = 1). The species of  $AB_7$  (e.g.  $IF_7$ ) and  $AB_6(lp)$  (e.g.  $XeF_6$ ) type have trigonal bipyramidal and distorted octahedral shapes respectively.

# Valence Bond Theory (VBT) of Covalent Bond

In order to explain how a covalent bond is formed Heitler and London in 1927 put forward a theory which is called *Valence Bond Theory (VBT)* or Atomic

Poslulates of VBT. According to this theory :

(i) An atomic orbital of the outermost shell of an atom containing one electron has a tendency to overlap with another atomic orbital of another atom containing one electron of opposite spin. This type of overlap gives rise to the formation of a bond which is called *covalent bond*. Thus :

According to atomic orbital theory a covalent bond between two atoms results by the overlap of half-filled atomic orbitals belonging to the outermost shell of these two atoms.

#### OR

The bond formed by the overlap of two atomic orbitals belonging to the outermost shell of two atoms and containing two electrons of opposite spin is called a covalent bond.

(*ii*) The overlap of two atomic orbitals gives rise to a single *bond orbital* which is a localised orbital and is occupied by both the electrons.

(iii) The two electrons that occupy the bond orbital have opposite spins.

(iv) Each electron occupies the entire bond orbital and hence may be considered to belong to both the atomic orbitals, *i.e.*, the electron pair present in the bond orbital now belongs to each of the two atomic orbitals.

(v) As a result of overlapping there is maximum electron density some where between the two atoms. A large part of the bonding force of covalent bond results from the electrostatic attraction between the nuclei and the accumulated electron clouds between them.

#### **Extension of VB Theory**

The above theory was extended by Pauling and Slater in 1931. According to the extension of this theory :

(i) The overlapping of orbitals involves a release of energy and hence the molecule formed has less energy and consequently is more stable than the isolated atoms. This implies that the formation of a covalent bond is always accompanied by the evolution of energy. The energy released as a result of overlapping of orbitals stabilises the system. The amount of energy released per mole at the time of overlapping of orbitals to form the covalent bond is termed as **bond energy** or **stabilisation energy**. This means that this much energy is required to separate the atoms in a molecule, *i.e.* to break the bond. The energy required to

#### Chemical Bonding (Orbital Concept)

break the bond in the molecule is called **bond dissociation energy**. The overlapping of atomic orbitals stops at a point where the atomic nuclei of both the atoms have come close enough to exercise a repulsive force on each other. Here the force of repulsion exactly balances the force of merger or attraction. The equilibirium distance at which the two atomic nuclei are now held is called **bond length**.

 $(\ddot{u})$  Overlapping takes place only between those valence- shell orbitals which have unpaired electrons. The orbitals containing paired electrons do not participate in overlapping process and hence do not contribute to bond formation.

(*iii*) Between the two orbitals of the same energy or stability, the orbital which is non-spherical (e.g. dumb-bell shaped p-orbital) forms stronger bonds than that which is spherically symmetrical (e.g. s-orbital).

(iv) A spherically symmetrical orbital does not show any preference in direction whereas the non-spherical orbitals tend to form a bond in the direction of maximum electron density within the orbital, *i.e.* along their axis.

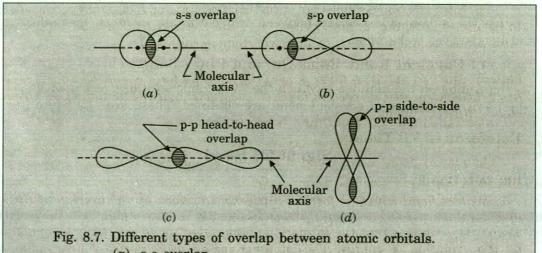
# **Types of Overlap of Atomic Orbitals**

Covalent bond between two atoms results by the following three types of overlap of atomic orbitals :

(i) s-s overlap. In this type of overlap half-filled s-orbital of one atom overlaps with the half filled s-orbital of the other atom [Fig. 8.7 (a)]

(ii) s-p overlap. Here half-filled s-orbital of one atom overlaps with the half-filled p-orbital of the other atom [Fig. 8.7 (b)].

(*iii*) **p-p overlap.** Here singly-filled *p*-orbital of one atom overlaps with the half-filled *p*-orbital of the other atom. Due to different spatial disposition of the *p*-orbital along the three cartesian coordinate axis the two *p*-orbitals may overlap in any of the following two ways :



- (a) s-s overlap
- (b) s-p overlap
- (c) p-p head-to-head overlap
- (d) p-p side-to-side overlap. Shaded portion contains an electron pair whose electrons have opposite spin.

(a) **p-p head-to-head overlap.** This is also called *head-on* or *end-on* or *end-to-end* or *linear overlap*. Here the overlap of the two p-orbitals takes place along the line joining the nuclei of two atoms (called *nuclear axis*, bond axis or molecular axis) [Fig. 8.7 (c)]. Hence the name linear overlap.

(b) **p-p side-to-side overlap.** This is also called *side-wise* or *side-way* or *lateral overlap*. Here the overlap of two p-orbitals takes place along a line perpendicular to the molecular axis. [Fig. 8.7 (d)]. Hence the name lateral overlap. This means that for this type of overlap the two p-orbitals must be held parallel to each other, *i.e.* the orbital axis should be parallel.

#### Strength of Covalent Bond—Effectiveness of Overlap

The strength of a covalent bond can be predicted from the following general conclusions.

(i) In the covalent bond formation, greater the extent of overlapping of orbitals, greater is the energy released, *i.e.* the higher will be the strength of the covalent bond. This implies that the strength of a covalent bond is proportional to the extent of overlapping between the atomic orbitals and that for a bond to be stronger, greater should be the overlap which in turn shortens the distance between the nuclei. Thus a stronger bond has a shorter bond length.

(ii) Bonding between two s-orbitals is weak particularly when two orbitals are of different energy (e.g. Li and K). Strongest bond between s-orbitals is between two 1s-orbitals of two H-atoms.

(*iii*) A strong bond is given by the head-to-head overlap of two *p*-orbitals which are of the same energy. The bond is much weaker, if the orbitals have different principal quantum numbers and bond energy becomes zero as the distance between the two levels increases. For example, C—Br bond in bromobenzene is much weaker than C—F bond in fluorobenzene.

(iv) The side-to-side overlap between two *p*-orbitals in much less effective and hence gives weak bond.

# Types of Covalent Bond: Sigma ( $\sigma$ ) and Pi ( $\pi$ ) Bonds

Depending on the manner in which the two atomic orbitals overlap with each other, two main types of covalent bond are obtained. These are : (i) Sigma ( $\sigma$ ) bond (also called a *single bond*) and (*ii*) *Pi* ( $\pi$ ) *bond*.

# Sigma (o) Bond

#### What is $\sigma$ Bond >

A covalent bond which is formed between two atoms by the overlap of their half filled atomic orbitals along the line joining the nuclei of both the atoms (i.e. along the nuclear axis, bond axis or molecular axis, as it is called) is called a  $\sigma$ -bond. In other words  $\sigma$ -bond is produced by the head-to-head overlap of the half filled atomic orbitals of the two atoms.

#### Characteristics of $\sigma$ -Bond.

 $\sigma$ -bond formed as above has the following characteristics :

(i) The boundary surface of  $\sigma$ -bond takes up an avoid shape.

(ii) The electron choud of this bond is symmetrical about the bond axis, i.e. the electron density in this bond is distributed symmetrically about the bond axis.

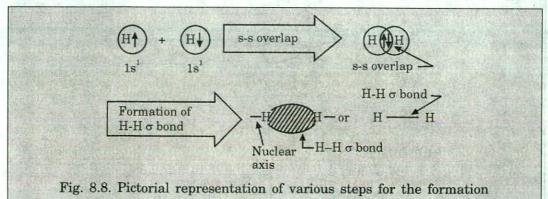
(iii) This bond has two electrons which have opposite spins. Although these two electrons may be present any where in the bond, the probability of their finding is maximum in the region between the two nuclei on the bond axis. Therefore they are attracted equally by the nuclei of both the atoms.

How this bond is formed between two atoms can be understood by considering the formation of covalent bonds in the molecules like  $H_2$ , HF,  $H_2O$ ,  $NH_3$  and  $F_2$  on the basis of atomic orbital overlap theory of covalent bond described above.

## Formation of o Bonds in Some Molecules

1.  $H_2$  molecule (s—s overlap). The two H-atoms of which  $H_2$  molecule is composed have 1s orbital each which contains only one electron  $(H \rightarrow 1s^1)$ . These 1s orbitals of both H-atoms approach each other closely and when they reach a point where the attractive forces (between electrons and nuclei) are balanced by the repulsive forces (between electrons and electrons, between the two nuclei), the potential energy becomes minimum, and hence they overlap and give rise to the formation of H—H  $\sigma$  bond. Since  $\sigma$  bond is produced by the overlap of two s-orbitals, it is also called s—s  $\sigma$ -bond. Thus a  $\sigma$  bond can be defined as

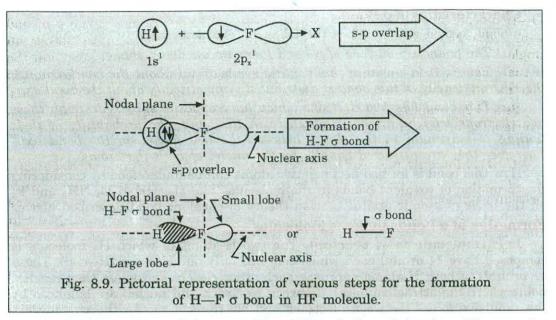
Various steps for the formation of a  $\sigma$ -bond in H<sub>2</sub> molecule are shown in Fig. 8.8.



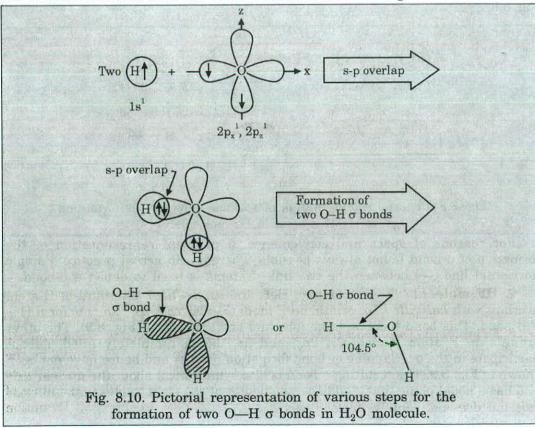
of H-H  $\sigma$  bond in H<sub>2</sub> molecule.

For reasons of space and convenience, a pictorial representation of the formation of  $\sigma$ -bond is not always possible. Therefore in actual practice a single horizontal line (—) between the two linked atoms is used to depict a  $\sigma$ -bond.

2. HF molecule (s—p overlap). Here the singly-filled 1s-orbital of H-atom overlaps with half-filled  $2p_x$  orbital on F atom  $(F \rightarrow 2s^2 2p_x^{-1} 2p_y^{-2} 2p_z^{-2})$  to form H—F  $\sigma$  bond. This bond has one large lobe and one small lobe (Fig. 8.9). The other orbitals on F atom namely 2s,  $2p_y$ , and  $2p_z$ , being completely filled, do not participate in the overlapping or bond formation process and hence have not been shown in Fig. 8.9. The resulting  $\sigma$  bond is also symmetrical about the nuclear axis and has a nodal plane that stands perpendicular at the right angles to the nuclear axis but does not contain nuclear axis.



**3.**  $H_2O$  molecule (*s-p overlap*). The valence shell configuration of O-atom *viz*.  $2s^2 2p_x^{-1} 2p_y^{-2} 2p_z^{-1}$  shows that it has two unpaired electrons. In the formation of  $H_2O$  molecule the half-filled  $2p_x$  and  $2p_z$  orbitals overlap with half-filled 2*s*-orbitals of two H-atoms and thus form two O—H  $\sigma$ -bonds as shown in Figure 8.10. Since these



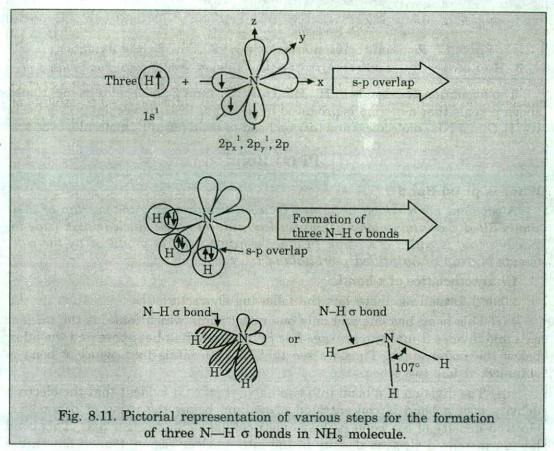
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#### Chemical Bonding (Orbital Concept)

O—H  $\sigma$ -bonds are produced by *s*-*p* overlap, these bonds are also called s-*p<sub>x</sub>* and s-*p<sub>z</sub>* bonds. Now since  $2p_x$  and  $2p_z$  orbitals are at right angles to each other, an angle of 90° between two O—H  $\sigma$ -bonds (*i.e.* H—O—H angle) is expected, but the actual angle is 104.5° instead of 90°. The increase in angle is due to the mutual electrostatic repulsion between the electron pairs constituting the two O—H bonds.

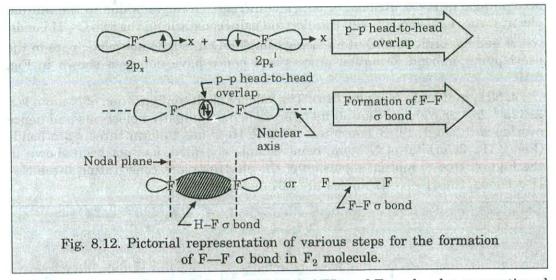
2s and  $2p_y$  orbitals of O-atom, being completely filled, do not participate in the overlapping or bond formation process and hence have not been shown in Fig. 8.10.

**4.** NH<sub>3</sub> molecule (s-p overlap). The valence shell configuration of N-atom viz.  $2s^2 2p_x^{-1} 2p_y^{-1} 2p_z^{-1}$  shows that all its p- orbitals have unpaired electrons and hence overlap with singly-filled 1s-orbitals of three H- atoms to form three s-p  $\sigma$  bonds (Fig. 8.11). 2s orbital of N atom, being completely filled, has not been shown in the Figure. Due to mutual repulsion of the electron pairs constituting three N—H  $\sigma$  bonds, the H—N—H angles are 107° instead of 90°.



5.  $\mathbf{F}_2$  molecule (*p-p head-to-head overlap*). Here *half-filled*  $2p_x$  orbital on one F atom (F  $\rightarrow 2s^2 2p_x^{-1} 2p_y^{-2} 2p_z^{-2}$ ) overlaps with similar *half-filled*  $2p_x$  orbital on the other F atom in a head-to-head fashion and forms F—F  $\sigma$  bond (Fig. 8.12), since the bond thus formed is symmetrical about the axis. 2s,  $2p_y$  and  $2p_z$  orbitals of both F atoms, being completely filled, do not participate in the bond formation

process and hence have not been shown in the Figure.  $\sigma$ -bond formed has two nodal planes which are perpendicular to the nuclear axis but do not contain the nuclear axis.



The formation of  $\sigma$ -bonds in H<sub>2</sub>, HF, H<sub>2</sub>O, NH<sub>3</sub> and F<sub>2</sub> molecules as mentioned above reveals that a  $\sigma$ -bond is produced by (i) s-s (as in H<sub>2</sub> molecule) (ii) s-p (as in HF, H<sub>2</sub>O and NH<sub>3</sub> molecules) and (iii) s-p head-to-head (as in F<sub>2</sub> molecule) overlaps.

## What is pi $(\pi)$ Bond ?

A covalent bond which is formed between two atoms by the overlap of their singly-filled p-orbitals along a line perpendicular to their nuclear axis (side-to-side overlap) is called a  $\pi$  bond. In other words  $\pi$  bond is produced by the side-to-side overlap of half-filled p-orbitals of the two atoms.

# Characteristics of $\pi$ -bond.

 $\pi$ -bond formed as above has the following characteristics.

(i) This bond has one and only one nodal plane which contains the nuclear axis and divides it into two sausage-like halves—one half lies above and the other below the nodal plane. Thus we see that like *p*-orbitals from which  $\pi$  bond is obtained, it has two lobes.

(*ii*) The division of  $\pi$  bond into two halves makes it evident that the electron density of a  $\pi$  bond is concentrated above and below the plane of  $\sigma$  bond *i.e.* electron density of a  $\pi$  bond is unsymmetrical about the nuclear axis. This bond has an increased electron density in the inter-nuclear region, though not on the bond axis.

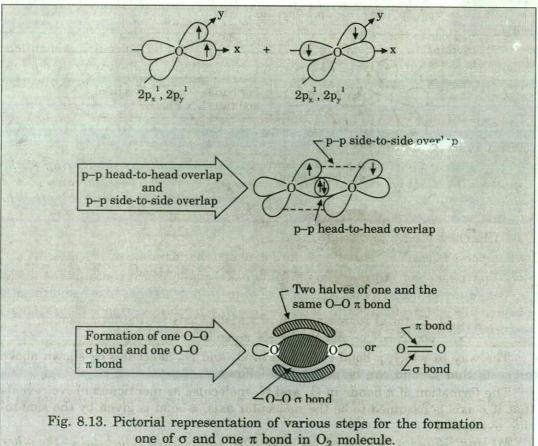
# Formation of $\pi$ Bonds in O<sub>2</sub> and N<sub>2</sub> Molecules

How this bond is formed can be understood by considering the formation of some simple molecules like  $O_2$  and  $N_2$  molecules.

**1.**  $O_2$  molecule (*p*-*p* head-to-head and *p*-*p* side-to-side overlaps). Valence shell configuration of O-atom viz.  $2s^2 2p_x 1 2p_y^{-1} 2p_z^{-2}$  shows that each of the O-atoms of  $O_2$  molecule has two singly filled *p*-orbitals namely  $2p_x$  and  $2p_y$  which are perpendicular to each other. Singly-filled  $2p_x$  orbitals on both O-atoms overlap in a head-to- head manner and form O—O  $\sigma$  bond while the remaining singlyfilled  $2p_y$  orbitals on both O-atoms are parallel to each other and hence overlap in a side-to-side manner to form a new type of bond around O—O  $\sigma$  bond which is called *pi* ( $\pi$ ) bond. The upper and lower overlaps of the two  $2p_y$  orbitals taken together constitute the  $\pi$  bond (Fig. 8.13).

Here it may be noted that 2s and  $2p_z$  orbitals of both O atoms, being completely filled, do not participate in bond formation or overlapping process and hence have not been shown in Figure 8.13.

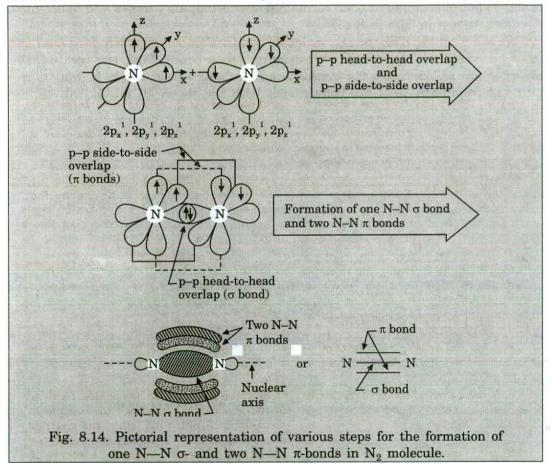
We see from Fig 8.13. that  $O_2$  molecule has two bonds one of which is a  $\sigma$ -bond  $(p_x-p_x \sigma \text{ bond})$  and the other is a  $\pi$ -bond  $(p_y-p_y \pi \text{ bond})$ . Both the bonds taken together are referred to as a *double bond*. Although both bonds ( $\sigma$  and  $\pi$ ) are different from each other, for convenience both are shown by two equal parallel lines.



2. N<sub>2</sub> molecule (*p-p head-to-head and p-p side-to-side overlaps*). The valence-shell configuration of N atom viz.  $2s^2 2p_x^{-1} 2p_y^{-1} 2p_z^{-1}$  shows that its all the

three *p*-orbitals are singly-filled and hence will participate in the bond formation with other N-atom. Singly filled  $2p_x$  orbitals of both N atoms overlap in a *headto-head manner* and form N—N  $\sigma$ -bond ( $p_x$ — $p_x \sigma$ -bond) while the remaining singlyfilled  $2p_y$  and  $2p_z$  orbitals of this N atom overlap with the similar *p*-orbitals of the other N atom in a *side-to-side manner* and form two N—N  $\pi$ -bonds ( $p_y$ — $p_y \pi$ -bond and  $p_z$ - $p_z \pi$ -bond) as shown in Fig. 8.14. Note that 2s orbital, being completely filled does not participate in bond formation and hence has not been shown in the Figure.

We see from Fig. 8.14. that N<sub>2</sub> molecule has three bonds one of which is a  $\sigma$ -bond ( $p_x-p_x \sigma$  bond) and the other two are  $\pi$ -bonds ( $p_y-p_y \pi$ -bond and  $p_z-p_z \pi$ -bond). All the three bonds taken together are referred to as a *triple bond*.



The way in which  $\pi$  bond is formed in  $O_2$  and  $N_2$  molecules as shown above suggests that  $\pi$ -bond can be defined as follows :

The formation of  $\pi$  bonds in O<sub>2</sub> and N<sub>2</sub> molecules as mentioned above reveals that if *x*-axis is assumed to be the molecular axis,  $\pi$ -bond is given by the side-to-side overlap of :

(a) singly-filled  $p_y$ -orbital of one atom with singly-filled  $p_y$ -orbital of the other atom  $(p_y-p_y \text{ overlap})$ .

(b) singly-filled  $p_z$ -orbital of one atom with singly-filled  $p_z$ -orbital of the other atom ( $p_z$ - $p_z$  overlap).

## Comparison of $\sigma$ - and $\pi$ -Bonds

The distinguishing features of a  $\sigma$ -bond from a  $\pi$ -bond are given in the following Table :

σ-Bond	π-Bond		
(i) A $\sigma$ -bond obtained by the <i>head-to-head</i> overlap <i>i.e.</i> (overlap of orbitals along the nuclear axis) of :	(i) If x-axis is assumed to be the nuclear axis, $\pi$ -bond is given by the <i>side-to-side</i> overlap ( <i>i.e.</i> overlap of orbitals along a line perpendicular to the nuclear axis) of :		
(a) two s-orbitals on two different atoms $(s-s \text{ overlap})$ .	(a) $p_y$ orbital of one atom with $p_y$ orbital of the other atom $(p_y-p_y \text{ overlap})$ .		
(b) one s-orbital of one atom with $p$ -orbital of the other atom ( $s-p$ overlap).	(b) $p_z$ orbital of one atom with $p_z$ orbital of the other atom $(p_z-p_z \text{ overlap})$ .		
(c) two p-orbitals on two different atoms $(p-p \text{ overlap})$ .	telefit in the same rate is the same rate		
( <i>ii</i> ) Since the extent of overlapping of orbitals along the nuclear axis is relatively greater than the extent of overlapping of orbitals along a line perpendicular to the nuclear axis, there is <i>more</i> decrease in energy of the molecule formed and hence $\sigma$ -bond is a stronger bond.	(ii) Since the side-wise overlap of two $p$ -orbitals which gives a $\pi$ -bond is partial, there is lesser <i>decrease</i> in energy of the molecule formed and hence $\pi$ -bond is a weaker bond.		
( <i>iii</i> ) In the formation of a $\sigma$ -bond by the overlap of two <i>p</i> -orbitals, only one lobe of one <i>p</i> -orbital of one atom overlaps with only one lobe of <i>p</i> -orbital of the other atom in a head-to-head manner.	(iii) In the formation of a $\pi$ -bond by the overlap of two <i>p</i> -orbitals, both lobes of both <i>p</i> -orbitals overlap with each other in a side-to-side manner.		
( <i>iv</i> ) The probability of finding the electrons between the two nuclei ( <i>i.e.</i> on the bond axis) is <i>maximum</i> , since they are attracted equally by both the nuclei. It is for this reason that $\sigma$ -bond is a very strong bond.	( <i>iv</i> ) The probability of finding the electrons between the two nuclei ( <i>i.e.</i> on the bond axis) is <i>poor</i> and hence $\pi$ -bond is a poor bond.		
(v) The electron density in this bond is distributed symmetrically about the nuclear axis.	(v) The distribution of electron density in this bond is <i>unsymmetrical</i> about the nuclear axis.		
(vi) There can be <i>free rotation</i> of the atoms relative to one another round the bond axis of $\sigma$ -bond ( <i>i.e.</i> nuclear axis).	(vi) There is no possibility of free rotation of the atoms relative to one another round the bond axis of $\pi$ -bond, since the electron clouds of <i>p</i> -orbitals of the two atoms overlap above and below the plane of the atoms. If an attempt to rotate the atoms relative to one another along the bond axis of $\pi$ -bond is made, the lobes of <i>p</i> -orbitals will no longer remain co-planar and the extent of overlapping of <i>p</i> -orbitals decreases, thus weakening the $\pi$ -bond still further. This property of restricted rotation in case of $\pi$ -bond is very useful in explaining the phenomena of cis-trans isomerism (geo- metrical isomerism).		

## **Concept of Resonance**

#### What is Resonance ?

Sometimes it is not possible to represent a molecule by a single valence bond structure which can correctly account for the properties of the molecule. In such cases valence bond method introduces the **resonance concept** according to which if two (or more) alternate valence bond structures can be written for a molecule, the actual structure of the molecule is said to be a **resonance** or **mesomeric hybrid** of all these alternate structures. For example, for  $H_2$  molecule this concept implies that neither structure (i) nor structure (ii) nor (iii) by itself provides a correct description of this molecule, but only a combination (i.e. hybrid) of the three structures (i), (ii) and (iii) or  $H_2$  molecule is a **resonance hybrid** of these three structures (i), (ii) and (iii) or  $H_2$  molecule is a **resonance hybrid** of these three structures (i), (ii) and (iii) or  $H_2$  molecule is a **resonance hybrid** of these three structures (i), (ii) and (iii) or  $H_2$  molecule is a **resonance hybrid** of these three structures (i), (ii) and (iii) or  $H_2$  molecule is a **resonance hybrid** of these three structures (i), (ii) and (iii) or  $H_2$  molecule is a **resonance hybrid** of these three structures (i), (ii) and (iii) or  $H_2$  molecule is a **resonance hybrid** of these three structures (i), (ii) and (iii) or  $H_2$  molecule is a **resonance hybrid** of these three structures (i).

 $\begin{array}{ccc} \stackrel{+}{H_A} \stackrel{-}{H_B} \leftrightarrow H_A - H_B \leftrightarrow H_A H_B \\ \hline Ionic & Covalent & Ionic \\ structure & structure & structure \\ (i) & (ii) & (iii) \end{array}$ 

This type of expression should not be taken to mean that  $H_2$  molecule sometimes has structure (i) and sometimes structures (ii) or (iii) and that the molecule oscillates between these three structures. The actual structure of the molecule is not a mixture of these three structures. Rather it is a single structure of its own, but as it cannot be written on paper, it is convenient to think of it in terms of the structures which can, of course, be written down on paper. The various structures of which the molecule is said to be a resonance hybrid are known as **contributing resonance** (or **canonical**) forms (or **extremes**) and have no physical reality *i.e.* these cannot be isolated. They are merely mental aids to rationalise the experimental behaviour of the molecules. Ingold has called the canonical forms as **mesomeric forms** or **mesomeric structures** and the conception is consequently known as **mesomerism** (between the parts).

To sum up :

Resonance is the description of the electronic structures of a molecule or an ion by means of several schemes of pairing of electrons, with the features of each scheme contributing in the description.

A double-headed arrow  $(\leftrightarrow)$  is placed between the different contributing forms to indicate that there is resonance between the various contributing structures.

Various structures of  $H_2$  molecule given above provide an example of *covalent*ionic resonance in one particular bond.

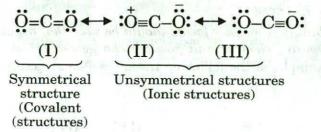
#### **Resonance Energy**

In a molecule which exhibits resonance it has been found that in every case the observed (i.e. experimental) heat of formation of the molecule is greater than the calculated heat of formation, i.e. the actual molecule is more stable than the

resonating structure considered for calculating the heats of formation. The resonating structure being used as the basis for calculating heats of formation must be the most stable of all the resonating structures among which resonance occurs. The difference between observed and calculated heat of formation is called **resonance energy**, usually represented as  $\Delta E$ . Thus  $\Delta E$  is the difference between the bond energy of the actual structure ( $E_{actual}$ ) and that of the most stable resonating structure.

## **Calculation of Resonance Energy**

Let us calculate the resonance energy of  $CO_2$  molecule which is supposed to be resonance hybrid of the following three structures.



Of these three resonating structures, structure (I) has the maximum bond energy and hence is the most stable. Thus resonance energy,  $\Delta E$  of CO<sub>2</sub> molecule relative to resonating structure (I) is given by :

Δ	$\mathbf{E} = \mathbf{E}_{actual}$	1.170	E <sub>1</sub>
	$= \begin{bmatrix} Experimental value of \\ heat of formation of CO_2 \end{bmatrix}$		Calculated value of heat of formation of structure (I)
	= 1602.8	140.00	$2 \times \text{Energy of C} = O \text{ bond (in KJ/mole)}$
	= 1602.8	-	2 × 732.3
	= 1602.8		1464.6
	199 9 la L/mala		and the second sec

= 138.2 kJ/mole.

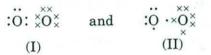
 $\Delta E$  (= 138.2 KJ/mole) is the energy lost when one molecule of CO<sub>2</sub> takes the resonance form (I). This also represents the additional energy which has to be supplied to disrupt the bonds due to their increased strength because of resonance. Resonance energy represents the extent to which the actual structure of CO<sub>2</sub> is more stable than the most stable resonating structure (I).  $\Delta E$  (= 138.2 KJ/molecule) stabilises the CO<sub>2</sub> molecule relative to the resonance form (I).

The calculated O—O bond distance in structure (I) is 2.44 Å while the experimental value is 2.30 Å. Thus we find that in the actual molecule (i.e., resonance hybrid) there is an increase in the value of heat of formation and shortening of bond lengths.

## **Requirements for Contributing Resonance Forms**

For the resonance to be possible the different canonical structures must satisfy the following conditions :

(i) The relative position of all the atoms in each of the resonance forms must be the same; the arrangement of electrons may differ. (ii) The number of unpaired and paired electrons in each of resonance forms must be the same so that a continuous change from one bond type to another may occur. For example,



cannot be the contributing structures of  $O_2$  molecule, since the number of paired and unpaired electrons in both the forms is different. Structure (II) contains two unpaired electrons and structure (I) does not contain any unpaired electron.

(iii) Contributing structures should be of comparable energy i.e. they should have almost equal energy.

(iv) Contributing resonance forms should be such that negative charge resides on an electronegative element and positive charge resides on an electropositive element. For example, of the following three possible structures (I), (II) and (III) of HF molecule,

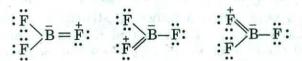
••	+	- ••
H - F:	HF:	HF:
 (I)		(III)
Covalent	Ionic structures	
structure		

structure (III) is ruled out, since in this structure negative charge resides on an electropositive element (H) and positive charge resides on an electronegative element (F). The actual structure of HF molecule is, therefore, considered to be a resonance hybrid of the structures (I) and (II) as shown below :

$$\begin{array}{ccc} H-F & \leftrightarrow & HF \\ (I) & (II) \end{array}$$

Structure (II) provides an example of *covalent-ionic resonance* in one particular bond.

(v) The greater the number of covalent bonds in a contributing structure, greater is the importance of that structure. For example since the structures of  $BF_3$  molecule shown below have double bond (B = F double bond), these are important.



In these structures it may be noted that F atom which is an electronegative atom acquires positive charge. This is contrary to rule (iv) given above. F atom acquires positive charge so that the electron deficiency of B atom is removed. The formation of an additional B = F double bond has a couter balancing effect.

## **Resonance Structures of Some Species**

1. CO molecule. See "Structure of CO molecule" given in this chapter.

2. CO<sub>2</sub> molecule. See "Structure of  $CO_2$  molecule" given in this chapter.

**3.**  $CO_3^{2-}$  ion. See "Structure of  $CO_3^{2-}$  ion" given in this chapter.

4.  $O_3$  molecule. See "Structure of  $O_3$  molecule" given in this chapter.

5. SO<sub>2</sub> molecule. See "Structure of  $SO_2$  molecule" given in this chapter.

6. SO<sub>3</sub> molecule. See "Structure of  $SO_3$  molecule" given in this chapter.

## **Concept of Promotion of Electrons**

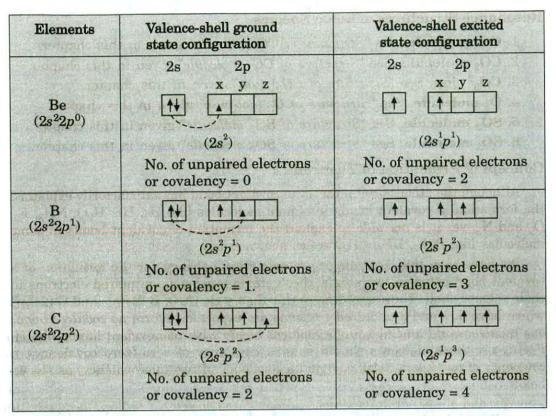
Although the atomic orbital theory of covalent bond has satisfactorily explained the formation of covalent bonds in simple molecules like  $H_2$ , HF,  $H_2O$ ,  $NH_3$ ,  $F_2$ ,  $O_2$  and  $N_2$ , yet it is not able to explain the formation of covalent bonds in some molecules like BeF<sub>2</sub>, BF<sub>3</sub>, CH<sub>4</sub> etc. as shown below.

We have seen that according to atomic orbital theory, for the formation of a covalent bond between two atoms, these atoms must have unpaired electrons in their valence-shell. Thus according to this theory Be  $(2s^2)$ , B  $(2s^2p^1)$  and C  $(2s^2p^2)$  which have 0, 1 and 2 unpaired electrons are expected to form *no covalent bond*, one covalent bond and two single covalent bonds with monovalent atoms like H, F etc., *i.e.* these elements should show a covalency of zero (zero covalency), a covalency of one (monocovalency) and a covalency of two (discovalency) as shown below :

Elements	Valence-shell ground state configuration	No. of unpaired electrons	Expected covalency or number of expected single covalent bonds	
Be $(2s^2)$	2s 2p	0	0	
$\mathbf{B}(2s^2p^1)$		at so type 1 per station	n de ser la siene de la ser	
$C(2s^2p^2)$		2	2	

However, the compounds of these elements show that these elements show a covalency of 2, 3 and 4 respectively. In other words these elements form the compounds like  $BeCl_2$  (covalency of B = 2),  $BCl_3$  (covalency of B = 3) and  $CH_4$  (covalency of C = 4).

In order to account for the covalency of 2, 3 and 4 for Be, B and C atoms, these elements should have 2, 3 and 4 unpaired electrons in their valence-shell respectively. This can be possible only when it is supposed that one of the 2s electrons is promoted to the next vacant higher energy 2p orbital as shown below :



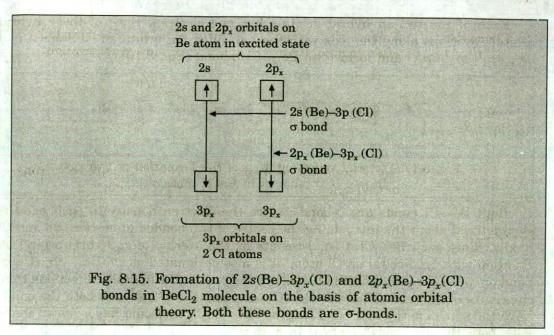
The above description which is based on the promotion of one of the two 2s electrons to the vacant higher energy 2p orbital well explains the covalency of 2, 3 and 4 of Be. B and C atoms.



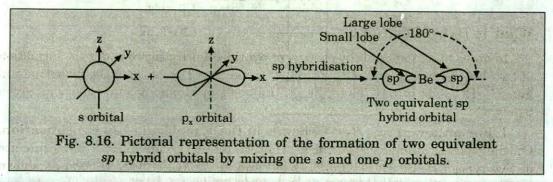
### What is Hybridisation ?

In order to understand the concept of hybridisation let us consider the formation of two Be—Cl bonds in BeCl<sub>2</sub> molecule, three B—Cl bonds in BCl<sub>3</sub> molecule and four C—H bonds in  $CH_4$  molecule on the basis of atomic orbital theory as given below :

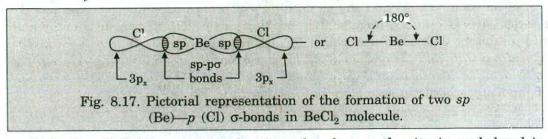
1. Formation of two Be—Cl bonds in BeCl<sub>2</sub> molecule—sp hybridisation. On the basis of atomic orbital theory the two Be—Cl bonds in BeCl<sub>2</sub> molecule are of two types : (i) 2s (Be)  $-3p_x(Cl)$  bond and (ii)  $2p_x(Be)-3p_x(Cl)$  bond as shown in Fig. 8.15. Both these bonds are  $\sigma$ -bonds. These are different in energy and hence different in length from each other. But experiments have shown that in BeCl<sub>2</sub> molecule both Be—Cl bonds have the same energy and same length and hence are identical to each other. These are directed in opposite direction along the axis of  $2p_x$  orbital, *i.e.* their arrangement round the Be atom



is linear and they make an angle of  $180^{\circ}$  with each other. Then how to account for the identical nature of Be—Cl bonds? For this it is assumed that 2s and  $2p_x$ orbitals of Be atom in the excited state mix or hybridise or merge together and redistribute their energy to give a set of two new equivalent (*i.e.* of the same energy and shape) orbitals which are known as sp hybrid orbitals because they are formed by the interaction of one s and one p orbital. These hybrid orbitals are also called sp orbitals and Be atom is said to be in sp hybridised state and the process of mixing one s and one p orbital to produce two equivalent (*identical*) sp hybrid orbitals is called **sp hybridisation**. The formation of two sp hybrid orbitals in case of Be atom is shown in Fig. 8.16.

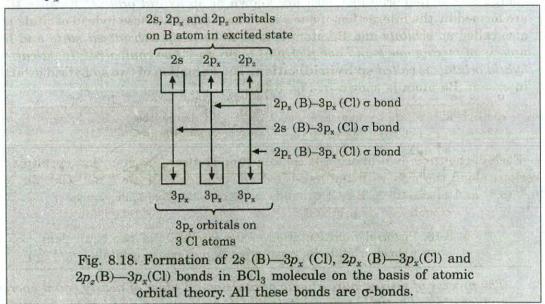


The process of mixing pure atomic orbitals on an atom of nearly equal energy to produce a set of entirely new orbitals which are equal in number to the mixing orbitals, have the same energy and identical shapes and are symmetrically disposed in space round the atom is known as hybridisation and the new orbitals produced are called hybrid orbitals or simply hybrids. The process of hybridisation is a hypothetical process. Each of the two *sp* hybrid orbitals has one electron. Each of these hybrid orbitals overlaps along the axis with the half-filled  $3p_x$  orbital of Cl atom (Cl  $\rightarrow$   $3s^2$ ,  $3p_x^{-1} 3p_y^{-2} 3p_z^{-2}$ ) and forms two Be— Cl  $\sigma$ -bond (Fig. 8.16).



Both Be—Cl bonds are  $\sigma$ -bonds, since the electron density in each bond is symmetrical about the line joining the centre of two bonded atoms *viz*. Be and Cl atoms. Since each Be—Cl  $\sigma$  bond results by the overlap of *sp* hybrid orbital on Be atom with  $3p_x$  orbital on Cl atom, it is also designated as sp (Be)— $3p_x$  (Cl)  $\sigma$ bond or sp— $p \sigma$ -bond. Both the bonds are directed in the opposite directions from the centre of Be atom. Thus Cl—Be—Cl bond angle is of 180° and both the bonds have the same energy and bond length. Thus BeCl<sub>2</sub> molecule has a linear shape with both Be—Cl bonds *identical* in nature.

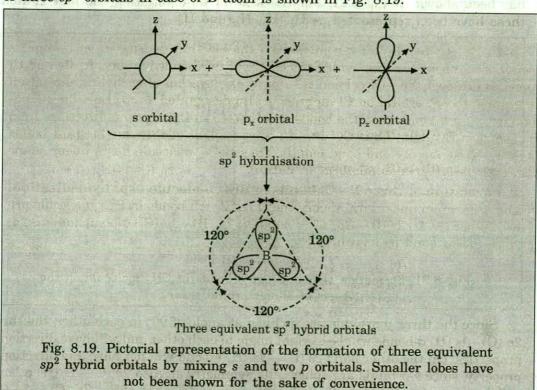
**2. Formation of three B—Cl bonds in BCl<sub>3</sub> molecule—sp<sup>2</sup> hybridization.** On the basis of atomic orbital theory the three B—Cl bonds in BCl<sub>3</sub> molecule are of three types *viz.* (*i*) 2s (B)— $3p_x$ (Cl)  $\sigma$  bond (*ii*)  $2p_x$ (B)— $3p_x$ (Cl)  $\sigma$ -bond and (*iii*)  $2p_z$ (B)— $3p_x$ (Cl)  $\sigma$  bond as shown in Fig. 8.18.



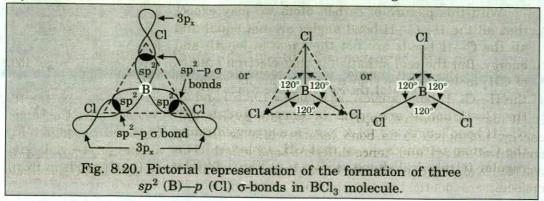
It may be seen that  $2p_x(B)$ — $3p_x(Cl)$  and  $2p_z(B)$ — $3p_x(Cl)$  bonds have the same energy and hence same bond length while 2s (B)— $3p_x(Cl)$  bond has different amount of energy and hence different bond length. Thus all the three bonds are not identical. But experiments have shown that all the three B—Cl bonds in BCl<sub>3</sub> molecule are identical and are inclined at an angle of 120° to each other, *i.e.* their

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arrangement round B atom is trigonal planar. Then how to explain the identical nature of B—Cl bonds? For this it is assumed that 2s,  $2p_x$  and  $2p_z$  orbitals of B atom in the excited state hybridise together to form a set of three new equivalent (*i.e.* of the same energy and shape) orbitals which are known as  $sp^2$  (read as esspec-two) hybrid orbitals, because they are formed by the interaction of one s and two p orbitals. These are also called  $sp^2$  orbitals and B atom is said to be in  $sp^2$  hybridised state and the process of mixing one s and two p orbitals to produce three equivalent (*i.e.* identical)  $sp^2$  hybrid orbitals is called  $sp^2$  hybridisation. The formation of three  $sp^2$  orbitals in case of B atom is shown in Fig. 8.19.

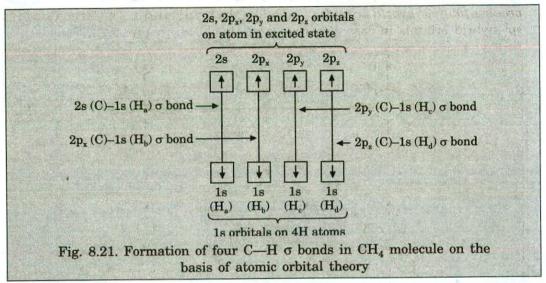


Each of the three hybrid orbitals contains one electron. Each of these orbitals overlaps along the axis with the half-filled  $3p_x$  orbital of Cl atom (Cl $\rightarrow$ 3s<sup>2</sup>,  $3p_x^1$   $3p_y^2$   $3p_z^2$ ) and forms three B—Cl  $\sigma$  bonds as shown in Fig. 8.20.



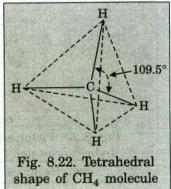
All the three B—Cl bonds are  $\sigma$  bonds. All the bonds are directed towards the corners of a triangular plane and hence each Cl—B—Cl bond angle is of 120° and all the bonds have the same bond length and energy. Thus BCl<sub>3</sub> molecule has a triangular shape with all the three B—Cl bonds *identical* in nature.

3. Formation of four C—H bonds in CH<sub>4</sub> molecule—sp<sup>3</sup> hybridisation. On the basis of atomic orbital theory the four C—H bonds in CH<sub>4</sub> molecule are of four types namely (i) 2s (C) —1s (H<sub>a</sub>)  $\sigma$ -bond (ii) 2p<sub>x</sub> (C) —1s (H<sub>b</sub>)  $\sigma$ -bond (iii) 2p<sub>y</sub> (C) —1s (H<sub>c</sub>)  $\sigma$  bond and (iv) 2p<sub>z</sub> (C)—1s(H<sub>d</sub>)  $\sigma$  bond. The formation of these bonds has been shown in Fig 8.21. For the sake of differentiating the four H-atoms these have been represented as H<sub>a</sub>, H<sub>b</sub>, H<sub>c</sub>, and H<sub>d</sub>.



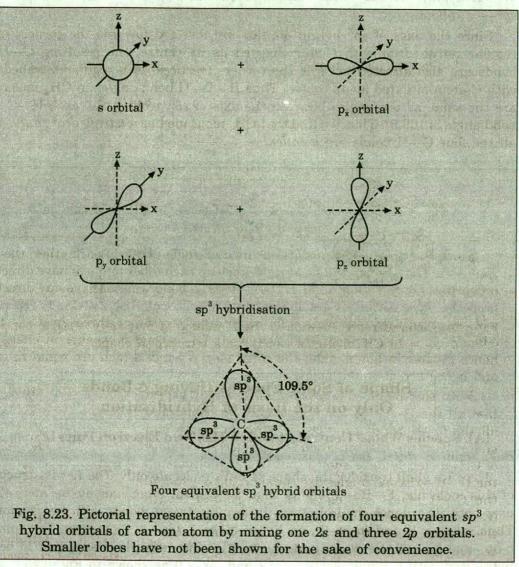
Since the three p-orbitals are inclined at angle of 90° to each other, the three 2p (C)—1s (H)  $\sigma$ -bonds will be at right angle to each other and will have directional properties. On the other hand 2s (C)—1s (H)  $\sigma$  bond will not have any directional property, since s-orbitals are spherically symmetrical. Also 2s (C)—1s (H)  $\sigma$  bond will be at an angle of about 125° with respect to other three 2p (C)—1s (H)  $\sigma$  bond hence greater in length than the three s-p  $\sigma$  bonds which are equal in energy and hence are of equal length.

With this picture of carbon atom we may expect that all the H—C—H bond angles are not equal and all the C—H bonds are not the same in length and energy. But the real situation is that electron studies of CH<sub>4</sub> molecule have shown that in this molecule all the H—C—H bond angles are equal (= 109.5°) and all the C—H bonds are equal in energy and length (C—H bond length = 1.09 A°) and are arranged round the C-atom tetrahedrally so that CH<sub>4</sub> molecule has a regular tetrahedral shape as shown in Fig. 8.22. The



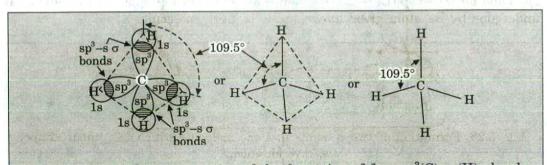
energy required to break any of the four bonds is the same (= 426.87 KJ mole<sup>-1</sup>). Thus all the C—H bonds in  $CH_4$  molecule are identical.

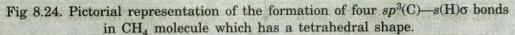
Then how account for the formation of four identical C—H bonds in  $CH_4$ molecule. For this it is assumed that the 2s and three 2p orbitals of carbon atom in the excited state mix or hybridise or merge together and redistribute their energy to give a set of four new equivalent (*i.e.* of the same energy and shape) orbitals which are known as  $sp^3$  (pronounced as ess-pee-three) hybrid orbitals because they are formed by interaction of one s and three p orbitals. These  $sp^3$ hybrid orbitals are also known as  $sp^3$  orbitals. Here carbon atom is said to be in  $sp^3$  hybridised state and the process of mixing one s and three p orbitals to produce four  $sp^3$  hybrid orbitals is called  $sp^3$  hybridisation. The formation of four  $sp^3$  hybrid orbitals in case of carbon atom is shown in Fig. 8.23.



All the four  $sp^3$  hybrid orbitals are identical, *i.e.*, they have the same energy and shape. These are directed towards the corners of a regular tetrahedron at the centre of which is placed the atom that has undergone  $sp^3$  hybridisation. Because of the tetrahedral disposition of  $sp^3$  hybrids,  $sp^3$  hybridisation is also called tetrahedral hybridisation and the four sp<sup>3</sup> hybrid orbitals are also called tetrahedral hybrid orbitals. Each of the four sp<sup>3</sup> hybrid orbitals on carbon atom is singlyfilled. Each of these hybrid orbitals overlaps along the axis with the half-filled 1s orbital on H-atom and forms four C-H σ bonds (See Fig. 8.24). All the four C-H bonds are  $\sigma$  bonds, since the electron density in each bond is symmetrical about the line joining the centre of two bonded atoms viz. C and H atoms. Since each C—H  $\sigma$  bond results by overlap of  $sp^3$  hybrid orbital on C-atom with 1s orbital  $sp^{3}(C) - s(H) \sigma$ -bond designated as or also on H-atom, it is  $sp^3 - s \sigma$ -bond.

Since the axes of  $sp^3$  hybrid orbitals are directed towards the corners of a regular tetrahedron with C-atom located as its centre, the resulting C—H  $\sigma$  bonds are also directed towards the corners (vertices) of a regular tetrahedron with C-atom situated at its centre. Thus H—C—H bond angles in CH<sub>4</sub> molecule are the same as the angles between the axis of  $sp^3$  orbitals, *i.e.* each H—C—H bond angle is 109.5°. Thus we find that CH<sub>4</sub> molecule has a *tetrahedral shape* and all the four C—H bonds are *identical*.

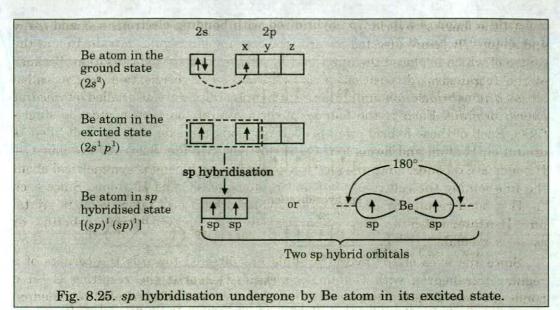




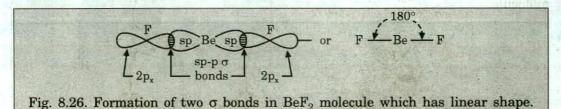
## Shape of Some Species Having σ-Bonds Only on the Basis of Hybridisation

## [A]. Species Whose Central Atom/Ion Has Two Electron Pairs [Examples : BeF<sub>2</sub> (molten state), BeCl<sub>2</sub> (gaseous)].

Here we shall consider the shape of BeF<sub>2</sub> molecule only. The Lewis structure of this molecule, F—Be—F shows that the central atom namely Be atom  $(2s^2)$ uses both its valence-shell electrons in forming two  $\sigma$ - bonds with two F atoms. Thus  $\sigma$ -bps = 2 and lps = 0 and hence  $\sigma$ -bps + lps = 2. Now since the sum of  $\sigma$ -bps and lps = 2, Be atom (central atom) in this molecule is supposed to be sp hybridised with bonding electrons = 2 and lps = 0 as shown in Fig. 8.25.



sp hybridisation scheme shown in Fig. 8.25 makes it evident that both the sp hybrid orbitals are singly-filled. These orbitals make a head-to-head (linear) overlap with the singly-filled  $2p_x$  orbitals on each of the two F atoms  $(F \rightarrow 2s^2, 2p_x^{-1} 2p_y^{-2} 2p_z^{-2})$  and form two sp (Be)— $2p_x(F)\sigma$  bonds as shown in Fig. 8.26. sp hybridisation undergone by Be atom gives linear shape to BeF<sub>2</sub> molecule.



#### [B]. Species Whose Central Atom/Ion Has Three Electron Pairs.

The species whose central atom is surrounded by three electron pairs may be of the following types :

(a)  $AB_3$  type. Here the central atom (A) is linked with three atoms (B) by  $\sigma$ -bonds and is surrounded by three  $\sigma$ -bps. Example are :  $BX_3(X = F, Cl, Br, I)$ ,  $BO_3^{3-}$  etc.

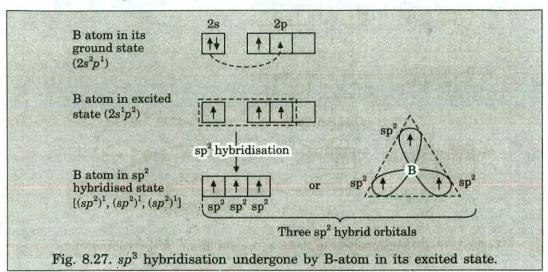
(b)  $AB_2(lp)$  type. The central atom is surrounded by two  $\sigma$ -bps and one lp. Examples are : gaseous SnCl<sub>2</sub>, PbCl<sub>2</sub> etc.

F

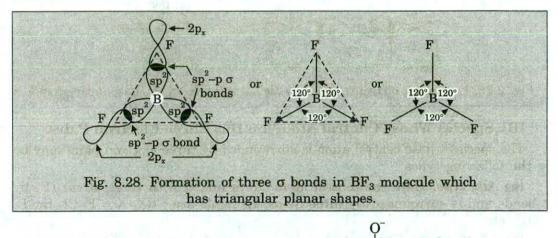
Here shall consider the shapes of BF<sub>3</sub>, BO<sub>3</sub><sup>3-</sup>, and SnCl<sub>2</sub> species.

**1. BF**<sub>3</sub> molecule. The Lewis structure of this molecule, F-B-F shows that the central atom namely B atom  $(2s^2p^1)$  uses all its valence-shell three electrons in forming three  $\sigma$ -bonds with three F atoms. Thus  $\sigma$ -bps = 3 and lps = 0 and hence  $\sigma$ -bps + lps = 3. Now since  $\sigma$ -bps + lps = 3, B atom (central atom) in this

molecule is supposed to be  $sp^2$  hybridised with bonding electrons = 3 and lps = 0 as shown in Fig. 8.27.

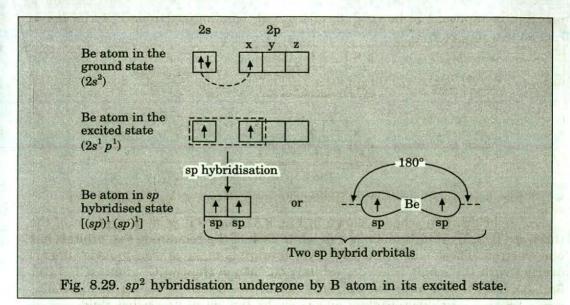


 $sp^2$  hybridisation scheme shown in Fig. 8.27 makes it evident that all the three  $sp^2$  hybrid orbitals are singly-filled. These orbitals make a *head-to-head* (*linear*) overlap with the singly-filled  $2p_x$  orbitals on each of the three F atoms  $(F \rightarrow 2s^2, 2p_x^{-1} 2p_y^{-2} 2p_z^{-2})$  and form three  $sp^2(B) - 2p_x(F) \sigma$ -bonds as shown in Fig. 8.28.  $sp^2$  hybridisation undergone by B atom gives a *triangular planar shape* to BF<sub>3</sub> molecule.

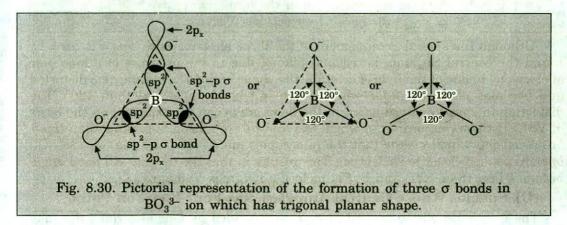


2.  $BO_3^{3-}$  ion. The Lewis structure of this ion is B which shows that the

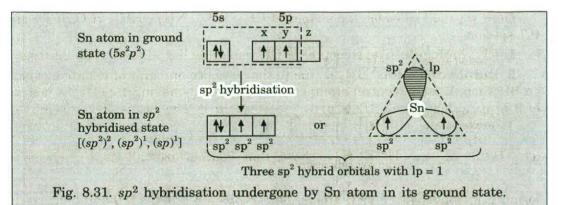
central atom namely B atom uses all its valence-shell three electrons  $(B \rightarrow 2s^2p^1)$ in forming three  $\sigma$  bonds with three O<sup>-</sup> ions. Thus  $\sigma$ -bps = 3 and lps = 0 and hence  $\sigma$ -bps + lps = 3. Now since the sum, bps + lps = 3, B atom (central atom) in BO<sub>3</sub><sup>3-</sup> ion is supposed to be  $sp^2$  hybridised with bonding electrons = 3 and lps = 0 as shown below in Fig. 8.29.



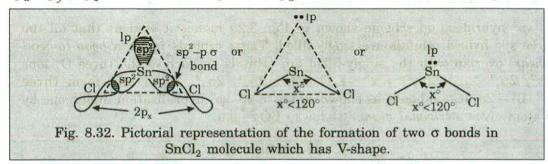
 $sp^2$  hybridisation scheme shown in Fig. 8.29 makes it evident that all the three  $sp^2$  hybrid orbitals are singly-filled. These orbitals make a *head-to-head* (*linear*) overlap with the singly-filled  $2p_x$  orbitals on each of the three O<sup>-</sup> ions  $(2s^2, 2p_x^{-1}, 2p_y^{-1}, 2p_z^{-2}) + e^- \rightarrow O^- (2s^2, 2p_x^{-1}, 2p_y^{-2}, 2p_z^{-2})]$  and form three  $sp^2$  (B)  $- 2p_x$  (O<sup>-</sup>)  $\sigma$  bonds as shown in Fig. 8.30.  $sp^2$  hybridisation undergone by B atom gives a *trigonal planar* shape to BO<sub>3</sub><sup>3-</sup> ion.



**3.** SnC1<sub>2</sub> molecule. The Lewis structure of this molecule, Cl–Sn–Cl shows that the central atom (*i.e.* Sn atom) uses only two electrons out of its four valence-shell electrons. (Sn  $\rightarrow 5s^2p^2$ ) in forming two  $\sigma$  bonds with 2Cl atoms while the remaining two electrons (*i.e.* one electron pair) remain as non-bonding electrons. Thus  $\sigma$ -ps = 2 and lps = 1 and  $\sigma$ -bps + lps = 3. Now since the sum of  $\sigma$ -bps and lps is 3, Sn atom (central atom) in SnCl<sub>2</sub> is supposed to be  $sp^2$  hybridised with bps = 2 and lps = 1 as shown in Fig. 8.31.



 $sp^2$  hybridisation scheme shown in Fig. 8.31 makes it evident that out of the three  $sp^2$  hybrid orbitals one has a lp while each of the remaining two orbitals has one electron. These singly-filled  $sp^2$  hybrid orbitals make a *head-to-head* (linear) overlap with the singly-filled  $3p_x$  orbitals on each of the two Cl atoms (Cl  $\rightarrow 3s^2$ ,  $3p_x^{-1} 3p_y^{-2}$ ,  $3p_z^{-2}$ ) and form two  $sp^2(\text{Sn})$ — $3p_x(\text{Cl}) \sigma$ —bonds as shown in Fig. 8.32.



Although the spatial arrangement of the three electron pairs (bps = 2, lps = 1), round the central Sn atom is trigonal planar, due to the presence of a lone pair of electrons in one of the hybrid orbitals, the shape of SnCl<sub>2</sub> molecule gets distorted and becomes *planar V-shape* with Cl—Sn—Cl bond angle less than 120°. The distortion in shape and reduction in the bond angle can be explained on the basis of VSEPR theory according to which the (lp-bp) repulsion is greater than (bpbp) repulsion which means that the lp occupies more space and the two (Sn—Cl) *bps* are pushed closer to each other. This results in that the Cl—Sn—Cl bond angle becomes less than 120° and SnCl<sub>2</sub> molecule becomes V-shaped.

#### [C]. Species Whose Central Atom/Ion Has Four Electron Pairs.

The molecules whose central atom is surrounded by four electron pairs may be of the following *four* types :

(a)  $AB_4$  type. Here the central atom (A) is surrounded by four  $\sigma$ -bps. Examples are : CH<sub>4</sub>, CX<sub>4</sub> (X = F, Cl, Br, I), SiCl<sub>4</sub>, BH<sub>4</sub><sup>-</sup>, AlH<sub>4</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, PH<sub>4</sub><sup>+</sup>.

(b)  $AB_3$  (lp) type. The central atom is surrounded by three  $\sigma$ -bps and one lp. Examples are : NH<sub>3</sub>, NF<sub>3</sub>, PX<sub>3</sub> (X = F, Cl, Br, I), PH<sub>3</sub>.

(c)  $AB_2$   $(lp)_2$  type. The central atom is surrounded by two  $\sigma$ -bps and two lps. Examples are : H<sub>2</sub>O, H<sub>2</sub>S, OX<sub>2</sub> (X = F, Cl, Br), SCl<sub>2</sub>, ICl<sub>2</sub>, NH<sup>-</sup><sub>2</sub>.

(d) AB  $(lp)_3$  type. The central atom is surrounded by one  $\sigma$ -bp and three lps. ICl molecule is an example of this type of molecules.

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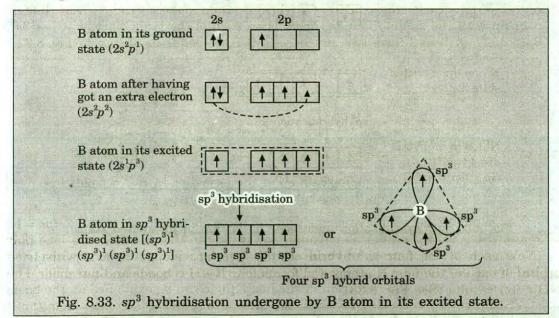
Here we shall consider the shapes of  $CH_4$ ,  $BH_4^-$ ,  $NH_4^+$ ,  $NH_3$ ,  $H_2O$ ,  $ICl_2^+$  and ICl species.

1. CH<sub>4</sub> molecule. The structure of CH<sub>4</sub> molecule has already been discussed.

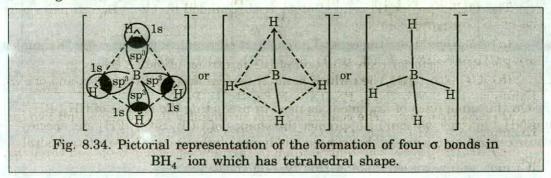
**2. Borohydride ion (BH**<sub>4</sub><sup>-</sup>). Due to the presence one unit of negative charge on  $BH_4^-$  ion, B atom (central atom) can be regarded as having 4 electrons instead of 3 in its valence-shell.  $[B(2s^2p^1)+e^- \rightarrow B^- (2s^2p^2)]$ . The Lewis structure of this

ion  $H = B^{-} = H$  or  $H^{?} = B^{?} = H$ , shows that B atom uses all its 4 electrons in H

forming  $4\sigma$  bonds with four H atoms. Thus  $\sigma$ -*bps* = 4 and *lps* = 0 and hence  $\sigma$ -*lps* + *lps* = 4. Consequently B atom is supposed to have undergone *sp*<sup>3</sup> hybridisation in the given ion as shown in Fig. 8.33.

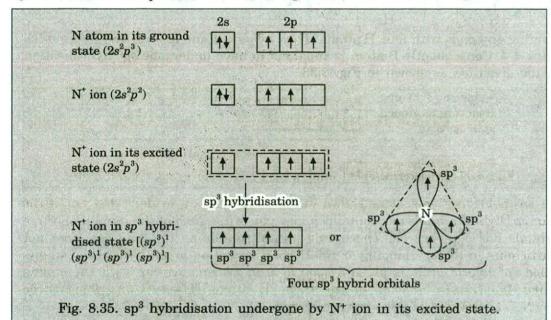


Each of the four  $sp^3$  hybrid orbitals on B atom is singly filled. Each of these hybrid orbitals overlaps along the axis with the half-filled 1s orbital on H-atom and forms four B—H  $\sigma$  bonds and consequently BH<sub>4</sub><sup>-</sup> ion has a tetrahedral shape (See Fig. 8.34).

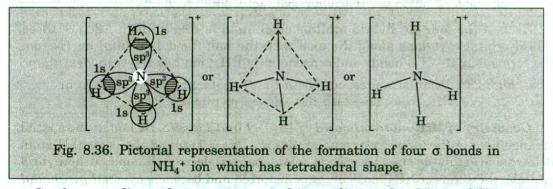


**3. Ammonium ion**  $(\mathbf{NH}_4^+)$ . Due to the presence of one unit of positive charge on  $\mathbf{NH}_4^+$  ion, N atom (central atom) can be regarded as having 4 electrons instead of 5 in its valence-shell  $[\mathbf{N}(2s^2p^3)-e^-\rightarrow \mathbf{N}^+(2s^2p^2)]$ . The Lewis structure of this ion,  $\begin{bmatrix} \mathbf{H} \\ \mathbf{H} \end{bmatrix} \begin{bmatrix} \mathbf{H} \\ \mathbf{H} \end{bmatrix}^+$ 

 $\begin{bmatrix} I \\ H-N^+-H \end{bmatrix}$  or  $\begin{bmatrix} \overline{I} \\ H-N-H \end{bmatrix}$  shows that N atom uses all its four electrons in forming four  $\sigma$  bonds with 4H atoms. Thus  $\sigma$ -bps = 4 and lps = 0 and hence  $\sigma$ -bps + lps = 4. Consequently N atom is supposed to have undergone sp<sup>3</sup> hybridisation in NH<sub>4</sub><sup>+</sup> ion as shown in Fig. 8.35.

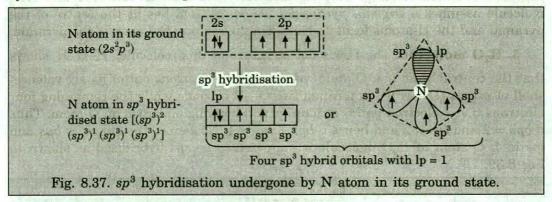


Now each of the four  $sp^3$  hybrid orbitals overlaps along the axis with 1s orbital of each of the four H atoms and forms four N—H  $\sigma$  bonds and tetrahedral NH<sub>4</sub><sup>+</sup> ion results (See Fig. 8.36).

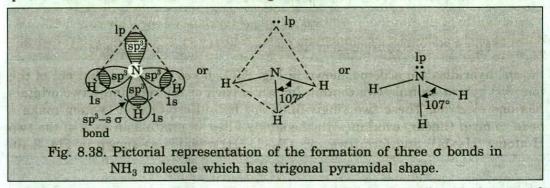


On the same lines of argument as used in predicting the shapes of  $CH_4$ ,  $BH_4^$ and  $NH_4^+$  species, we can also, predict the shapes of  $CCl_4$ ,  $SiCl_4$ ,  $PH_4$  etc. species whose central atoms are  $sp^3$  hybridised and hence all the species have a tetrahedral shape. 4. NH<sub>3</sub> molecule. The Lewis structure of this molecule, H-N-H shows that

the central atom (*i.e.* N atom) uses only three electrons. Out of its five valenceshell electrons  $(N \rightarrow 2s^2p^3)$  three are used up in forming 3 $\sigma$  bonds with 3H atoms while the remaining two electrons (*i.e.* one electron pair) remain as non-bonding electrons on N-atom. Thus  $\sigma$ -bps = 3 and lps = 1 and  $\sigma$ -bps + lps = 4. Now since the sum of  $\sigma$ -bps and lps is 4, N atom in NH<sub>3</sub> molecule is supposed to be sp<sup>3</sup> hybridised as shown in Fig. 8.37.



 $sp^3$  hybridisation scheme shown in Fig. 8.37 makes it evident that out of the four  $sp^3$  hybrid orbitals one contains a lone pair while each of the remaining three orbitals has one electron. The hybrid orbital containing the lone pair does not participate in the overlapping or N—H bond formation process while the singly-filled  $sp^3$  hybrid orbitals make a *head-to-head* (*linear*) overlap with the singly-filled 1s orbitals on each of the three H atoms  $(H\rightarrow 1s^1)$  and form three  $sp^3(N)$ —1s (H)  $\sigma$  bonds as shown in Fig. 8.38.

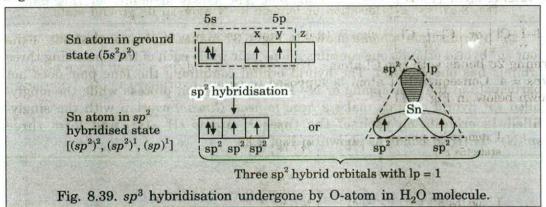


Geometry of  $NH_3$  molecule and  $H_N_H$  bond angle. Although the spatial arrangement of the four electron pairs (bps = 3, lps = 1) round the central N atom is tetrahedral, due to the presence of a lone pair of electrons in one of the hybrid orbitals, the shape of  $NH_3$  molecule gets distorted and becomes trigonal pyramidal and each of three  $H_N_H$  bond angles decreases from the expected tetrahedral angle (= 109.5°) to 107°. The distortion in shape and hence reduction in the bond angle can be explained on the basis of VSEPR theory according to which, since lp belongs to N-atom only, the hybrid orbital containing the lp occupies more

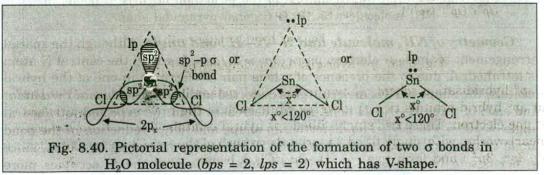
space than the other three hybrid orbitals each of which contains a lp and belongs to three H-atoms and one N-atom jointly. The greater spread in space of the hybrid orbital containing the lp results in that a lp repells a bp more strongly than a bp repells another bp, *i.e.*  $(lp\_bp)$  repulsion becomes greater than  $(bp\_bp)$  repulsion. The net effect of this difference in the electron pair—electron pair repulsions is that the lone pair on N-atom forces the three (N—H) bps to come closer to each other and hence each of H—N—H bond angle decreases from tetrahedral angle (= 109.57) to 107°. Due to the decrease in the bond angle, the expected tetrahedral shape of NH<sub>3</sub> molecule gets a little distorted and NH<sub>3</sub> molecule assumes a *trigonal pyramidal shape*. N-atom lies at the centre of the pyramid and the H-atoms form its base. The lp occupies the apex of the pyramid.

5. H<sub>2</sub>O molecule. The Lewis dot structure of this molecule, H-O-H shows

that the central atom (*i.e.* O atom) uses only two electrons out of its six valenceshell electrons  $(O \rightarrow 2s^2p^4)$  in forming two O—H  $\sigma$  bonds while the remaining four electrons (*i.e.* 2 electron pairs) remain as non-bonding electrons on O-atom. Thus  $\sigma$ -bps = 2 and lps = 2 and hence  $\sigma$ -bps + lps = 4. Now since the sum of  $\sigma$ -bps and lps is 4, O-atom in H<sub>2</sub>O molecule is supposed to be  $sp^3$  hybridised as shown in Fig. 8.39.



 $sp^3$  hybridisation scheme shown in Fig. 8.39 makes it evident that out of the four  $sp^3$  hybrid orbitals two contain *lps* while each of the remaining two orbitals has one electron. These two singly-filled  $sp^3$  hybrid orbitals on O-atom make a *head-to-head* (linear) overlap with the singly-filled 1s orbitals on each of the two H-atoms (H $\rightarrow$ 1s<sup>1</sup>) and form two  $sp^3$  (O)—1s (H)  $\sigma$  bonds as shown in Fig. 8.40.



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Geometry of  $H_2O$  molecule and H—O—H bond angle. Although the spatial arrangement of the four electron pairs (bps = 2, lps = 2) round the central O-atom is tetrahedral, due to the presence of two lone pairs of electrons in two hybrid orbitals, the shape of  $H_2O$  molecule gets distorted and becomes V-shape (angular or bent shape), and H—O—H bond angle decreases form the expected tetrahedral angle (= 109.5°) to 104.5°. The distortion in shape and decrease in bond angle can be explained on the basis of VSEPR theory according to which the distortion in shape and decrease in H—O—H bond angle is due to the presence of two lps on O-atom and the difference in the magnitude of three types of electron pair electron pair repulsions shown below :

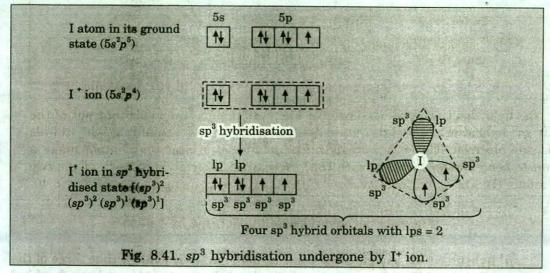
## (lp-lp) repulsion > (lp-bp) repulsion > (bp-bp) repulsion

The net effect of the difference in the magnitude of electron pair—electron pair repulsions shown above is that the two lps on O-atom force the two (O—H) bps to come closer to each other and hence each of the H—O—H bond angles in  $H_2O$  becomes less than the tetrahedral angle (= 109.5°) and  $H_2O$  molecule assumes V-shape which is a distorted shape of a tetrahedron.

6. [ICl<sub>2</sub>]<sup>+</sup> ion. Due to the presence of one unit of positive charge on the ion, I atom (central atom) can be regarded as having six electrons instead of seven in its valence-shell [I  $(5s^2p^5)-e^- \rightarrow I (3s^2p^4)$ ]. The Lewis structure of this ion,

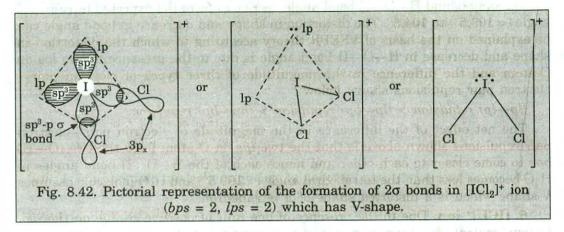
 $\begin{bmatrix} Cl-I-Cl \end{bmatrix}$  or  $\begin{bmatrix} Cl-I-Cl \end{bmatrix}^+$  shows that I atom uses two of its six electrons in

forming  $2\sigma$  bonds with two Cl atoms. Thus  $\sigma$ -bps = 2 and lps = 2 and hence  $\sigma$ -bps + lps = 4. Consequently I atom is supposed to be sp<sup>3</sup> hybridised in ICl<sub>2</sub><sup>+</sup> ion as shown below in Fig. 8.41.

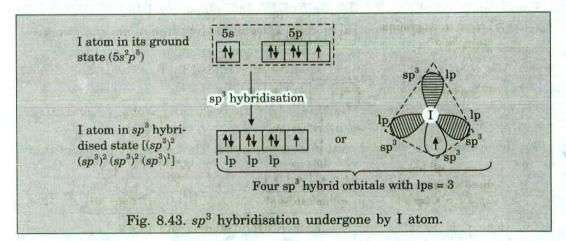


 $sp^3$  hybridisation scheme shown in Fig. 8.41 makes it evident that out of the four  $sp^3$  hybrid orbitals two contain lps while each of the remaining two orbitals has one electron. These two singly-filled  $sp^3$  hybrid orbitals make a *head-to-head* (linear) overlap with singly-filled  $3p_x$  orbitals on each of the two Cl atoms. (Cl $\rightarrow$ 3s<sup>2</sup>,  $3p_x^1 3p_y^2 3p_z^2$ ) and form two  $sp^3$  (I)-3 $p_x$  (Cl)  $\sigma$  bonds.

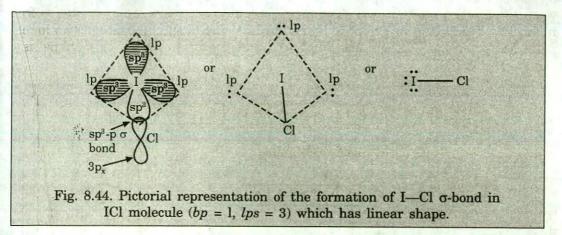
Although the spatial arrangement of four electron pairs (bps = 2, lps = 2) round the central I atom in space is tetrahedral, due to the presence of two lone pairs, the shape of  $ICl_2^+$  ion gets distorted and becomes angular or V-shape as shown in Fig. 8.42.



7. ICl molecule. The Lewis structure of this molecule, :I-Cl shows that the central atom (*i.e.* I atom) uses only one of its seven valence-shell electrons  $(I \rightarrow 5s^2p^5)$  in forming 1 $\sigma$  bond with one Cl atom while the remaining six electrons (*i.e.*, 3 electron pair) remain as non-bonding electrons on I-atom. Thus  $\sigma$ -bps = 1 and lps = 3 and  $\sigma$ -bps + lps = 4. Now since the sum of  $\sigma$ -bps and lps is 4, I atom in ICl molecule is supposed to be  $sp^3$  hybridised as shown in Fig. 8.43.



 $sp^3$  hybridisation scheme shown in Fig. 8.43 makes it evident that three of the four  $sp^3$  hybrid orbitals contain one lp each while the fourth  $sp^3$  hybrid orbital contains one electron. This singly-filled  $sp^3$  hybrid orbital makes a *head-to-head* (*linear*) overlap with the singly-filled  $3p_x$  orbital on Cl atom and forms one  $sp^3(I)$ — $3p_x$  (Cl)  $\sigma$  bond as shown in Fig. 8.44.



Although the spatial arrangement of the four electron pairs (bp = 1 and lps = 3) round the central I atom is tetrahedral, due to the presence of three lone pairs of electrons in three hybrid orbitals, the shape of ICl molecule gets distorted and becomes linear.

## [D] Species Whose Central Atom/Ion Has Five Electron Pairs.

The molecules whose central atom is surrounded by five electron pairs may be of the following *four* types :

(a)  $AB_5$  type. Here the central atom (A) is surrounded by five  $\sigma$ -bps. Example are :  $PX_5$  (X = F, Cl, Br) and SbF<sub>5</sub> (all in gaseous phase).

(b)  $AB_4$  (lp) type. Here the central atom is surrounded by four  $\sigma$ -bps and one lp. Examples are : SF<sub>4</sub>, SeF<sub>4</sub>, TeF<sub>4</sub> (all in gaseous phase) and IF<sub>4</sub><sup>+</sup>.

(c)  $AB_3 (lp)_2$  type. The central atom is surrounded by three  $\sigma$ -bps and two lps. Examples are ClF<sub>3</sub>, BrF<sub>3</sub>, IF<sub>3</sub>.

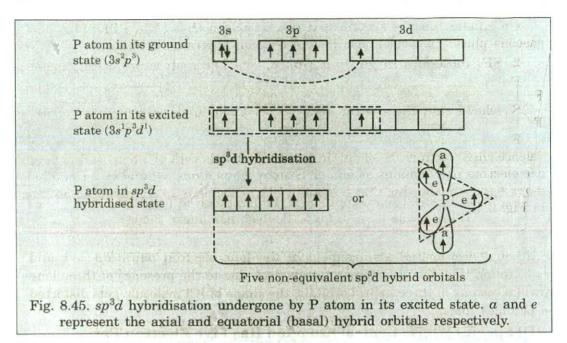
(d)  $AB_2$   $(lp)_3$  type. The central atom is surrounded by two  $\sigma$ -bps and three lps. Examples are : XeF<sub>2</sub>, I<sub>3</sub><sup>-</sup>, ICl<sub>2</sub><sup>-</sup>.

Here we shall consider the shape of  $PF_5$ ,  $SF_4$ ,  $IF_4^+$ ,  $CIF_3$ ,  $XeF_2$ ,  $I_3^-$  and  $ICl_2^-$  species.

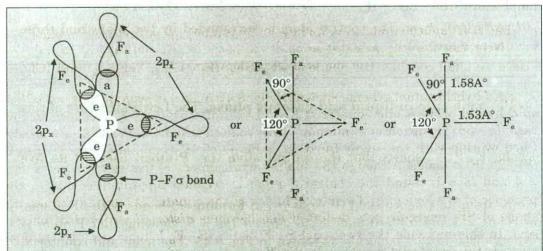
1. PF5 molecule in liquid and gaseous phase. The Lewis structure of this

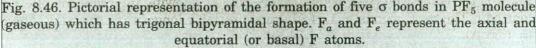
molecule,  $F \stackrel{F}{\underset{F}{\overset{F}{\xrightarrow{}}}} F$  shows that the central atom (*i.e.* P atom) uses all its five

electrons from its valence-shell  $(P \rightarrow 3s^2p^3)$  in forming 5 $\sigma$  bonds with 5F atoms. Thus  $\sigma$ -bps = 5 and lps = 0 and hence  $\sigma$ -bps + lps = 5, showing that P-atom is  $sp^3d$  hybridised in this molecule as shown in Fig. 8.45. The axial and equatorial (basal) hybrid orbitals have been shown by a and e respectively.



 $sp^3d$  hybridisation scheme shown in Fig. 8.45 makes it evident that each of the five hybrid orbitals is singly-filled. These hybrid orbitals overlap with  $2p_x$  orbital of 5F atoms  $(F\rightarrow 2s^2, 2p_x{}^1.2p_y{}^2.2p_z{}^2)$  and form five  $sp^3d(P)-2p_x$  (F)  $\sigma$  bonds as shown in Fig. 8.46 and PF<sub>5</sub> has a trigonal bipyramidal shape. In this molecule the three equatorial bonds (P-F<sub>e</sub> bonds) are equal in length but shorter than the two axial bonds (P-F<sub>a</sub> bonds). This is because of the fact that the axial P-F<sub>a</sub> bonds are less strong than the equatorial P-F<sub>e</sub> bonds. This confirms that the five  $sp^3d$  hybrid orbitals are non-equivalent.





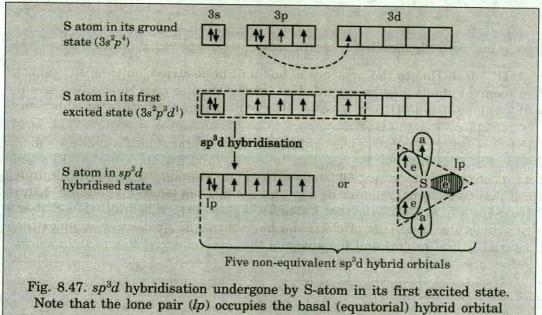
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On similar lines of argument it can be shown that  $PCl_5$ ,  $PBr_5$ ,  $SbF_5$  (all in gaseous phase) molecules also have a trigonal bipyramidal shape.

2. SF<sub>4</sub> molecule in gaseous phase. The Lewis structure of this molecule F

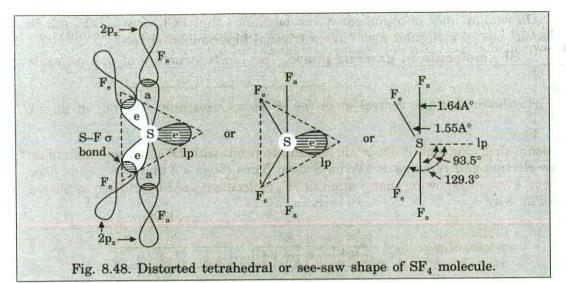
F S: shows that the central atom (*i.e.* S atom) uses only four out of its six

valence-shell electrons  $(S \rightarrow 3s^2p^4)$  in forming 4 $\sigma$  bonds with 4F atoms and remaining one electron pair remains as a lp on S atom. Thus  $\sigma$ -bps = 4 and lp = 1 and hence  $\sigma$ -bps + lps = 5, showing that S atom in SF<sub>4</sub> molecule is  $sp^3d$  hybridised as shown in Fig. 8.47.



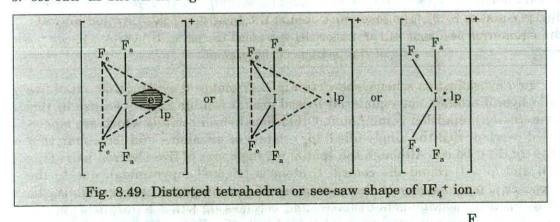
of the pentagonal bipyramid.

 $sp^{3}d$  hybridisation scheme shown in Fig. 8.47 makes it evident that out of five  $sp^{3}d$  hybrid orbitals one equatorial hybrid orbital contains a lp, because in this case (lp-bp) repulsion is minimum. Other four hybrid orbitals which are singly-filled overlap with the singly-filled  $2p_{x}$  orbitals of 4F atoms and form four  $sp^{3}d$  (S)— $2p_{x}(F) \sigma$  bonds. Although the spatial arrangement of five electron pairs (bps = 4 and lp = 1) round the central S atom is trigonal bipyramidal, due to the presence of one lone pair of electrons in one of the equatorial hybrid orbitals, the shape of SF<sub>4</sub> molecule gets distorted and becomes distorted tetrahedral or see-saw. In this molecule the two axial S—F bonds (S—F<sub>a</sub> bonds) are slightly bent towards the equatorial S—F bonds, (S—F<sub>e</sub> bonds), showing the repulsion effect of lone pair. The S—F<sub>a</sub> bonds (= 1.64 Å) are appreciably longer than the S—F<sub>e</sub> bonds (= 1.55 Å).



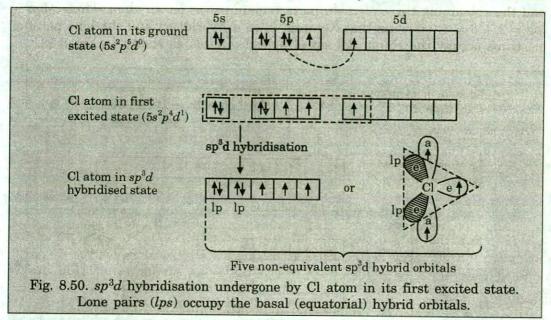
3. IF<sub>4</sub><sup>+</sup> ion. Due to the presence of one unit of positive charge on IF<sub>4</sub><sup>+</sup> ion, I atom (central atom) may be regarded as having six electrons (instead of seven) in its valence-shell  $[I(5s^2p^5)-e^- \rightarrow I(5s^2p^4)]$ . Lewis structure of this ion,

 $\begin{bmatrix} F & F \\ F & F \end{bmatrix}$  or  $\begin{bmatrix} F & F \\ F & F \end{bmatrix}^{+}$  shows that the central atom (*i.e.* I atom) uses four of its six electrons in forming 4 $\sigma$  bonds with 4F atoms and remaining one electron pair (*i.e.* two electrons) remains as a lp on I atom. Thus  $\sigma$ -bps = 4 and lp = 1 and hence  $\sigma$ -bps + lp = 5, showing that I atom in IF<sub>4</sub><sup>+</sup> ion is  $sp^3d$  hybridised as S atom in SF<sub>4</sub> molecule. Lone pair of electrons, like that in SF<sub>4</sub> molecule, occupies the equatorial hybrid orbital and the shape of the ion becomes distorted tetrahedral or see-saw as shown in Fig. 8.49.

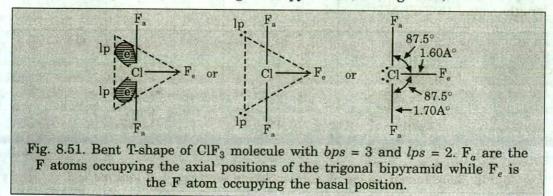


4. ClF<sub>3</sub> molecule. The electronic structure of this molecule, F-Cl-F shows that the central atom namely Cl atom uses three out of its seven valence-shell electrons in forming 3 $\sigma$  bonds with 3F atoms while the remaining four electrons

(*i.e.* two electron pairs) are left as lps on Cl atom. Thus  $\sigma$ -bps + lps = 3 + 2 = 5 and hence Cl atom in ClF<sub>3</sub> molecule can be supposed to be  $sp^3d$  hybridised as shown in Fig. 8.50. The lps occupy the equatorial hybrid orbitals.

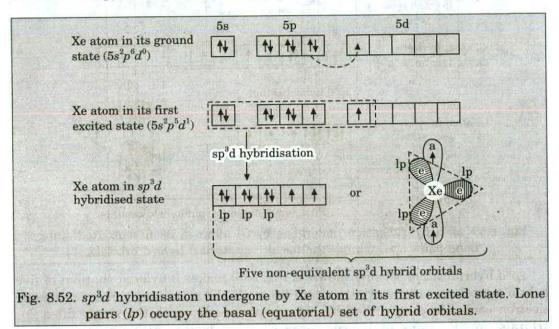


 $sp^3d$  hybridisation scheme shown in Fig. 8.50 makes it evident that out of five hybrid orbitals two (equatorial) contain lps while the remaining three contain one electron each. The singly-filled hybrid orbitals overlap with the singly filled  $2p_x$ orbitals on 3F atoms and form three Cl—F  $\sigma$  bonds. Although the spatial arrangement of five electron pairs (bps = 3, lps = 2) round the central Cl atom in space is trigonal bipyramidal, due to the presence of two lone pairs, the shape of ClF<sub>3</sub> molecule gets distorted and becomes *slightly bent T-shape* with bond angles equal to 87.5°. The lone pairs occupy the hybrid orbitals directed towards the equatorial positions of the trigonal bipyramid (See Fig. 8.51).

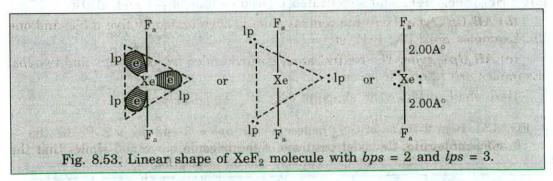


On similar grounds if can be shown that  $BrF_3$  and  $IF_3$  both have T-shaped structure. In  $BrF_3$  the axial bonds ( $Br-F_a = 1.81$  Å) are appreciably larger than the equatorial bonds ( $Br-F_b = 1.72$  Å). Such parameters for  $IF_3$  are not known.

5. XeF<sub>2</sub> molecule. The Lewis structure of this molecule, F-Xe-F shows that the central atom (*i.e.* Xe atom) uses two electrons in forming two Xe—F  $\sigma$  bonds and the remaining three electron pairs remain as lps on Xe atom. Thus  $\sigma$ -bps + lps = 2 + 3 = 5, showing that Xe atom is  $sp^3d$  hybridised and the lone pairs of electrons occupy the equatorial set of hybrid orbitals as shown in Fig. 8.52.

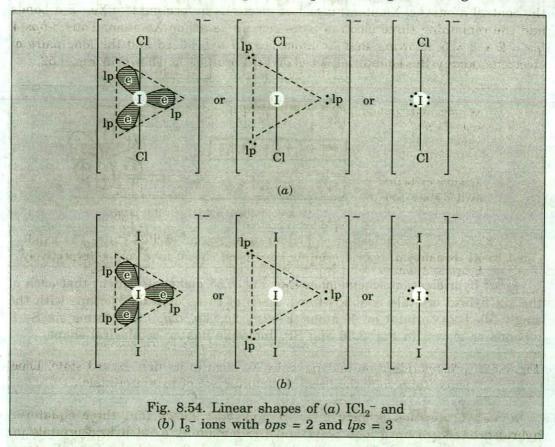


 $sp^{3}d$  hybridisation scheme given in Fig. 8.52 shows that three equatorial hybrid orbitals (e) have lone pairs and the remaining axial hybrid orbitals (a) have one electron each. These orbitals overlap with  $2p_{x}$  orbitals of two F atoms  $(F \rightarrow 2s^{2}, 2p_{x}^{-1} 2p_{y}^{-2} 2p_{z}^{-2})$  and form two Xe—F  $\sigma$  bonds. Due to the presence of lps, XeF<sub>2</sub> molecule assumes a *linear shape* as shown in Fig. 8.53 with Xe—F bond lengths equal to 2.00 A°.



**6.**  $ICl_2^-$  and  $I_3^-$  ions. On the same lines of argument as used in case of XeF<sub>2</sub>, it can be shown that both  $ICl_2^-$  and  $I_3^-$  ions are also linear in shape. In both the ions, due to the presence of one unit of negative charge, the central atom namely

I atom is regarded as having eight electrons  $[I(5s^2p^5) + e^- \rightarrow I^- (5s^2p^6)]$  (instead of seven). The linear shapes of  $ICl_2^- =$  and  $I_3^-$  ions are given in Fig. 8.54.



## [E] Species Whose Central Atom/Ion Has Six Electron Pairs

The molecules of this type may be of the following three types :

(a)  $AB_6$  type. Here the central atom (A) is surrounded by six  $\sigma$ -bps. Examples are : SF<sub>6</sub>, SeF<sub>6</sub>, TeF<sub>6</sub> and substituted molecules like SF<sub>5</sub>Cl and SF<sub>5</sub>Br.

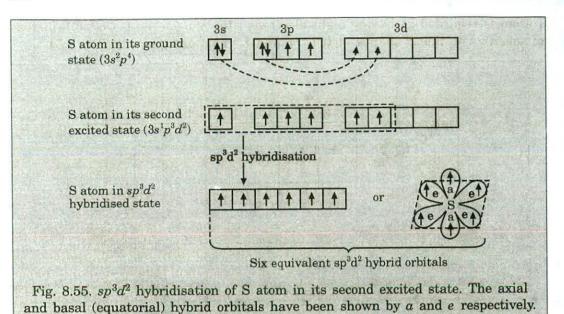
(b)  $AB_5(lp)$  type. Here the central atom is surrounded by five  $\sigma$ -bps and one lp. Examples are : IF<sub>5</sub>, BrF<sub>5</sub> etc.

(c)  $AB_4(lp)_2$  type. The central atom is surrounded by four  $\sigma$ -bps and two lps. Examples are : XeF<sub>4</sub>, ICl<sub>4</sub><sup>-</sup> etc.

Here shall consider the shape of  $SF_6$ ,  $IF_5$ ,  $XeF_4$  molecules.

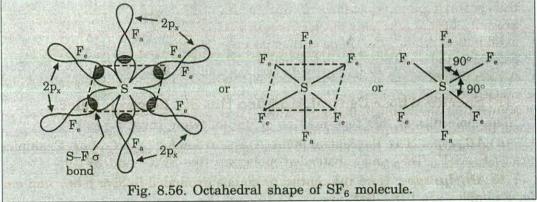
1. SF<sub>6</sub> molecule. Lewis structure of this molecule,  $F \xrightarrow{F}_{F} \xrightarrow{F}_{F}$  shows that the

central atom namely S atom uses all its six valence-shell electrons in forming six S—F  $\sigma$ -bonds. Thus  $\sigma$ -bps = 6 and lps = 0 and hence  $\sigma$ -bps + lps = 6, showing that S atom is  $sp^3d^2$  hybridised in this molecule as shown in Fig. 8.55.



 $sp^{3}d^{2}$  hybridisation scheme shown in Fig. 8.55 makes it evident that each of the six hybrid orbitals is singly-filled. Each of these orbitals overlaps with the

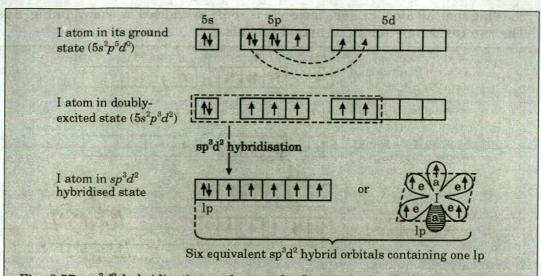
singly-filled  $2p_x$  orbital on F atom (F $\rightarrow$ 2s<sup>2</sup>,  $2p_x^{-1}.2p_y^{-2}.2p_z^{-2}$ ) and forms six S—F  $\sigma$ -bonds as shown in Fig. 8.56 and SF<sub>6</sub> molecule has an octahedral shape.

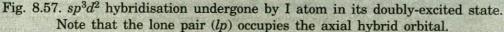


On the similar lines of arguement it can be shown that  $SeF_6$ ,  $TeF_6$ ,  $SF_5CI$  and  $SF_5Br$  molecules also have octahedral shape.

## 2. IF<sub>5</sub> molecule in vapour state. Lewis structure of this molecule,

shows that the central atom namely I atom uses only five out of its seven valenceshell electrons  $(I \rightarrow 5s^2p^5)$  in forming five I—F  $\sigma$ -bonds and the remaining one electron pair remains as a lp on I atom. Thus  $\sigma$ -bps = 5 and lp = 1 and hence  $\sigma$ -bps+ lps = 6, showing that I atom in IF<sub>5</sub> molecule is  $sp^3d^2$  hybridised as shown in Fig. 8.57 The lp occupies the axial hybrid orbital.





 $sp^{3}d^{2}$  hybridisation shown in Fig. 8.57 makes it evident that out of six  $sp^{3}d^{2}$ hybrid orbitals one axial hybrid orbital contains a lp, because in this case the (lp-bp) repulsion is minimum. Other five hybrid orbitals which are singly-filled overlap with singly-filled  $2p_x$  orbitals of 5F atoms and form five I-F  $\sigma$ -bonds. Although the spatial arrangement of six electron pairs (bps = 5 and lp = 1) round

the central I atom is octahedral, due to the presence of one lone pair of electrons in the axial hybrid orbital, the shape of IF5 molecule gets distorted and becomes square pyramidal. A recent single crystal structure study of this molecule made by Burbank and Jones has shown that the basal F atoms (F, atoms) are slightly displaced upwards from the base of the square pyramid and hence IF5 molecule assumes the structure as shown in Fig. 8.58.  $F_a IF_e$  bond angle has been found to be equal to 81.9°. I— $F_a$  bond distance (= 1.73 A°) is appreciably shorter than the I-Fe bond distance (= 1.87 A°).

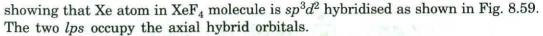
⊢1.73 A° 1.87 A 81.9° F, lp Fig. 8.58. Square pyramidal structure of IF<sub>5</sub> molecule.

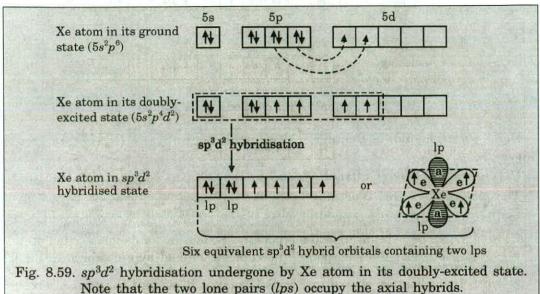
On the basis of similar arguements it can be shown that ClF<sub>5</sub> and BrF<sub>5</sub> molecules also have square pyramidal shape.

# 3. XeF<sub>4</sub> molecule. Lewis structure of this molecule, $\stackrel{F}{\xrightarrow{}} \stackrel{Xe}{\xrightarrow{}} \stackrel{F}{\xrightarrow{}}$ shows that

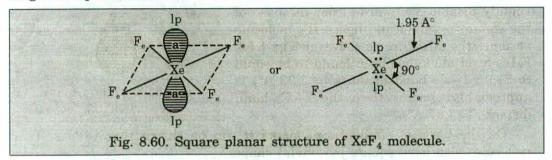
the central atom namely Xe atom uses only four of its eight valence-shell electrons  $(Xe \rightarrow 5s^2p^6)$  in forming four Xe—F  $\sigma$ -bonds and the remaining two electron pairs remain as lps on Xe atom. Thus  $\sigma$ -bps = 4 and lps = 2 and hence  $\sigma$ -bps + lps = 6,

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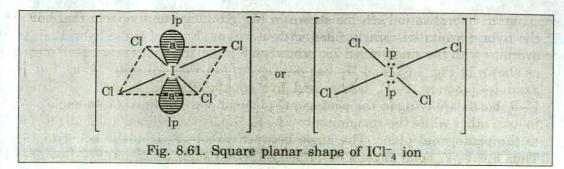




 $sp^3d^2$  hybridisation shown in Fig. 8.59. makes it evident that out of six  $sp^3d^2$  hybrid orbitals two axial hybrid orbitals contain two lps, because, in order to have minimum lone pair repulsion, the lone pairs must be as far from each as possible. Other four hybrid orbitals (equatorial hybrid orbitals) which are singly-filled overlap with singly-filled  $2p_x$  orbitals of 4F atoms and form four Xe—F  $\sigma$ -bonds. Although the spatial arrangement of six electron pairs (bps = 4 and lps = 2) round the central Xe atom is octahedral, due to the presence of two lps in the axial hybrid orbitals, the shape of XeF<sub>4</sub> gets distorted and becomes square planar as shown in Fig. 8.60.  $F_e$ —Xe— $F_e$  angle has been found to be equal to 90° and Xe— $F_e$  bond length is equal to 1.95 A°.



On the basis of similar arguments it can be shown that  $ICl_4^-$  ion (I is the central atom) also has a square planar shape as depicted in Fig. 8.61. Due to the presence one unit of negative charge on the ion, I atom (central atom) is supposed to contain eight electrons (instead of seven) in its valence-shell  $[I(5s^2p^5) + e^- \rightarrow I^- (5s^2p^6)]$ . Four electrons are used to from four I—Cl  $\sigma$ -bonds and four electrons (*i.e.* two electron pairs) remain as *lps* on I atom.



 $\mathrm{BrF}_4^-$  (central atom is Br) and  $\mathrm{IF}_4^-$  (central atom is I) ions have analogous shapes.

## [F] Species Whose Central Atom/Ion Has Seven Electron Pairs

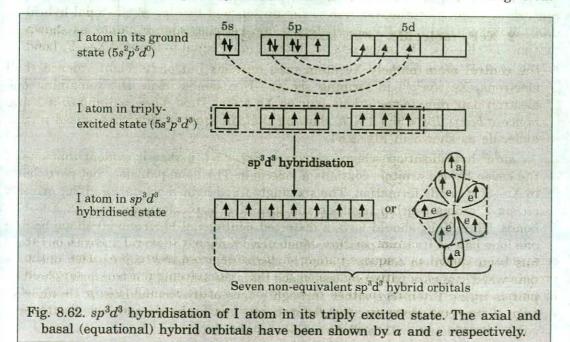
The molecules of this type may be of the following two types :

(a)  $AB_7$  type. Here the central atom (A) is surrounded by seven  $\sigma$ -bps. IF<sub>7</sub> is an important example of this type of molecules.

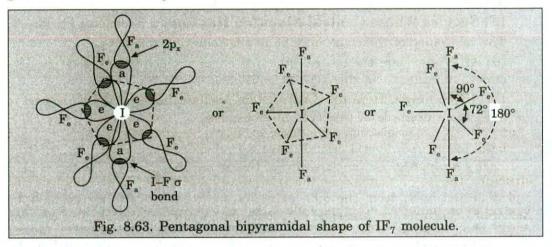
(b)  $AB_6(lp)$  type. Here the central atom is surrounded by six  $\sigma$ -bps and one lp. XeF<sub>6</sub> is an example of this type of molecules.

1. IF<sub>7</sub> molecule. Lewis structure of this molecule,  $\stackrel{F}{F} \rightarrow \stackrel{I}{I} \stackrel{F}{\searrow} \stackrel{F}{F}$  shows that the

central atom namely I atom uses all its seven valence-shell electrons in forming seven I—F  $\sigma$ -bonds. Thus  $\sigma$ -bps = 7 and lps = 0 and hence  $\sigma$ -bps + lps = 7, showing that I atom is  $sp^3d^3$  hybridised in this molecule as shown in Fig. 8.62.



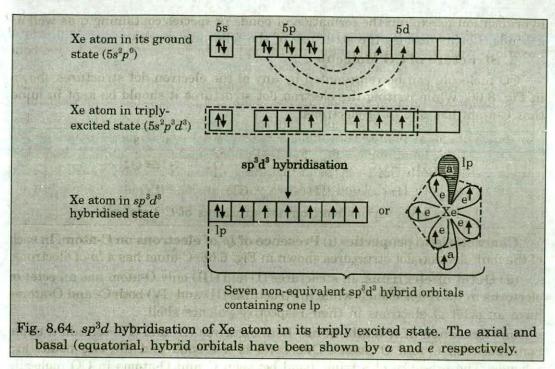
 $sp^3d^3$  hybridisation scheme shown in Fig. 8.62. makes it evident that each of the hybrid orbitals is singly filled with electrons. Each of these hybrid orbitals overlaps with the singly-filled  $2p_x$  orbital on F atom and forms seven I—F  $\sigma$  bonds as shown in Fig. 8.63. and IF<sub>7</sub> has *pentagonal bipyramidal shape* which has two axial I—F bonds (I—F<sub>a</sub> bonds) and five equatorial I—F bonds (I—F<sub>e</sub> bonds). I—F<sub>e</sub> bonds are lying in the pentagonal plane and are inclined at an angle of 72° to each other while the remaining two I—F<sub>a</sub> bonds are inclined at an angle of 90° to the pentagonal plane. The angle between two I—F<sub>a</sub> bonds is equal to 180°. Thus F<sub>a</sub>—I—F<sub>e</sub> bond angle = 90°, F<sub>e</sub>—I—F<sub>e</sub> bond angle = 72° and F<sub>a</sub>—I—F<sub>a</sub> bond angle = 180°. Both the I—F<sub>a</sub> bond distances which are equal to each other are greater than both I—F<sub>e</sub> bond distances which are again equal to each other.



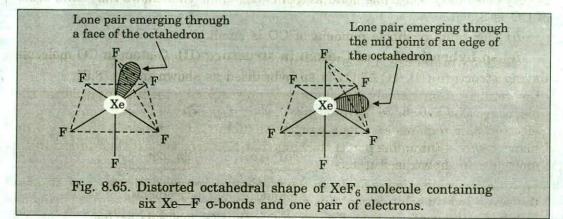
2. XeF<sub>6</sub> molecule. Lewis structure of this molecule,  $F \downarrow F$ F-Xe F-Xe F-Xe

the central atom namely Xe atom uses only six out of its eight valence shell electrons  $(Xe \rightarrow 5s^2p^6)$  in forming six Xe—F  $\sigma$  bonds while the remaining one electron pair remains as a lone pair on Xe atom. Thus  $\sigma$ -bps = 6 and lp = 1 and hence  $\sigma$ -bps + lps = 6 + 1 = 7, showing that Xe atom is  $sp^3d^3$  hybridised in this molecule as shown in Fig. 8.64.

 $sp^3d^3$  hybridisation scheme shown in Fig. 8.64. makes it evident that one of the seven hybrid orbitals contains a lone pair. This lone pair does not participate in Xe—F  $\sigma$  bonds formation. The six singly-filled hybrid orbitals and  $2p_x$  orbitals on six F atoms overlap together and give rise to the formation of six Xe—F  $\sigma$ bonds. Thus XeF<sub>6</sub> should have a distorted pentagonal bipyramidal shape having one lone pair at its axial position. Monomeric XeF<sub>6</sub> in the liquid and gaseous state has been shown to contain a *slightly distorted octahedral shape* with one lone pair which appears to occupy less space than the bonding electron pair. The lone pair is trying to emerge either through a face of the octahedron or through an edge of the octahedron (See Fig. 8.65). In the latter case the molecule would have some resemblance with a distorted pentagonal bipyramid (cf IF<sub>7</sub>). In either



structure, the Xe—F bonds near the lone pair appear to be somewhat lengthened and distorted away from the lone pair. The fact that  $XeF_6$  forms adducts like  $XeF_6.SbF_5$  confirms the presence of a lone pair in the valence-shell of Xe atom.



A cubic phase of XeF<sub>6</sub> studied at  $-80^{\circ}$ C contains XeF<sub>5</sub><sup>+</sup> and F<sup>-</sup> ions that are associated in tetrameric and hexameric rings.

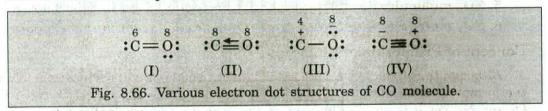
Shape of Species Having  $\sigma$  As Well As  $\pi$  Bonds On the Basis of Hybridisation.

So far we have used the concept of hybridisation to explain the shape of the species containing only  $\sigma$  bonds. In this section we shall use the concept of

hybridisation to explain the formation of bonds in species containing  $\sigma$  as well as  $\pi$  bonds. Let us discuss the structure of the following species :

## 1. Structure of CO Molecule.

CO molecule can be represented by any of the electron dot structures shown in Fig. 8.66. While writing the electron dot structures it should be kept in mind that C-atom has one lp of electrons.



Characteristic properties (i) Presence of lp of electrons on C-atom. In each of the four electron dot structures shown in Fig. 6.66. C-atom has a lp of electrons.

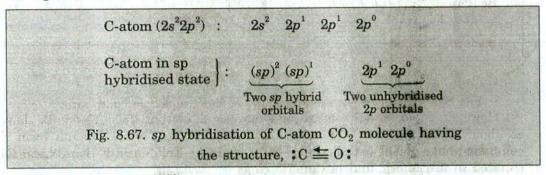
(ii) Octet of electrons. In structures (I) and (III) only O-atom has an octet of electorns in its valence shell while in structures (II) and (IV) both C- and O-atoms have an octet of electrons in their respective valence shell.

(*iii*) **Presence of a triple bond**. Both structres (II) and (IV) contain a triple bond between C and O atoms. One bond is a  $\sigma$ -bond and the two bonds are  $\pi$ -bonds. The presence of a triple bond between C and O-atoms in CO molecule is supported by the following facts.

(a) The bond length between C and O-atoms in CO molecule is  $1.128 \text{ A}^{\circ}$  which is very close to C = O triple bond length (=  $1.10 \text{ A}^{\circ}$ ). This shows that bond order of CO is 3.

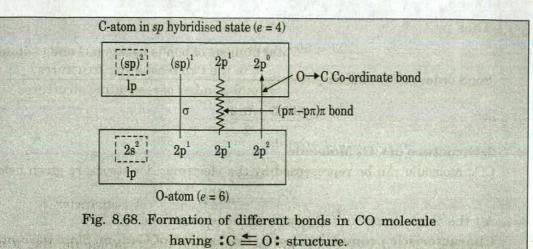
(b) The value of dipole moment of CO is small.

(*iv*) sp hybridisation of C-atom in structure (II). C-atom in CO molecule having structure (II), :C  $\leq$  O: is sp hybridised as shown in Fig. 8.67.



It may be seen that two 2p orbitals remain unhybridised.

(v) Formation of different bonds in CO molecule. Formation of different bonds in CO molecule has been shown in Fig. 8.68.  $(C - O) \sigma$  bond is obtained by the overlap of sp hybrid orbital of C-atom with 2p orbital of O-atom.  $(C - O) \pi$  bond is obtained by the overlap between 2p orbital on C and O atoms. Thus  $(C - O) \pi$  bond is a  $(p\pi - p\pi) \pi$  bond.  $O \rightarrow C$  coordinate bond is a  $[2p^2(O) \rightarrow 2p^0(C)]$  bond.



(vi) **Resonance in CO molecule.** X-ray diffraction study of CO molecule has shown that carbon-oxygen bond length in this molecule is equal to 1.13 A°. This exprimentally determined value is niether equal to the calculated value of  $C \equiv O$ triple bond length (= 1.10 A°) nor equal to C = O double bond length (= 1.22 A°) or C - O single bond length (= 1.43 A°). Thus the true structure of CO molecule is the resonance hybrid of the following resonating structures.

Dipole moment of CO is very small (= 0.12 D)

Since the exprerimental value of carbon-oxygen bond length in CO (=  $1.13 \text{ A}^{\circ}$ ) is very close to the calculated value of C = O triple bond length (=  $1.10 \text{ A}^{\circ}$ ), the true structure of CO is generally regarded as a resonance hybrid of the following resonating structures.

$$: C \stackrel{-}{\equiv} 0: \longleftrightarrow : \stackrel{-}{C} \stackrel{+}{\equiv} \stackrel{+}{0}:$$
(II) (IV)

(vii) Acting as Lewis base or ligand. Due to the presence of lp of electrons on C-atom, CO molecule acts as a Lewis base or a Ligand in metal carbonyls. The lp of electrons is used in forming metal  $\leftarrow$  carbon coordinate bond in carbonyls

 $\begin{pmatrix} 1 & 0 \\ M \leftarrow \overline{C} \equiv 0 \end{pmatrix} = 1 (d, d) = p (d$ 

(ix) Bond order (B.O). We have already said that the true structure of CO molecule is generally regarded as a resonance hybrid of the two resonating structures (given below) containg triple bond between C and O atoms.

$$\begin{array}{c} :C \triangleq 0: \longleftrightarrow :C \equiv 0: \\ (II) & (IV) \end{array}$$

Thus :

Total number of bonds between C and O atoms in the two resonating structures

Bond order of CO molecule = \_\_\_\_\_ Total number of resonating structures

$$=\frac{3+3}{2}=\frac{6}{2}=3$$

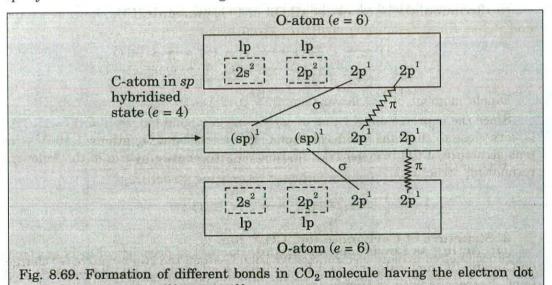
## 2. Structure of CO<sub>2</sub> Molecule

CO<sub>2</sub> molecule can be represented by the electronic dot structure given below.

$$: \ddot{o} = c = \ddot{o}:$$

All the three atoms in  $CO_2$  molecule obey octet rule.

**Characteristic properties** (i) sp hybridisation of C-atom. Since the central C-atom is surrounded by two  $\sigma$ -bonds and no lp of electrons, this atom in its excited state (C in excited state =  $2s^1 2p^3$ ) is sp hybridised. In sp hybridisation, two 2p orbitals of C-atom remain unhybridised and form two (C - O)  $\pi$  bonds with two O-atoms. Both  $\pi$  bonds are  $(p\pi - p\pi) \pi$  bonds. The formation of two (C - O)  $\sigma$  bonds and two (C - O)  $\pi$  bonds in CO<sub>2</sub> molecule by sp hybridisation is shown in Fig. 8.69



structure,  $\ddot{0} = C = \ddot{0}$ ; by the use of sp hybridisation.

(*ii*) Linear shape of  $CO_2$  molecule. Due to sp hybridisation of C-atom and absence of lp of electrons on C-atom,  $CO_2$  molecule has linear shape. Thus  $CO_2$  is *linear monomeric covalent molecule*. Both carbon-oxygen bond lengths are equal to 1.15 A°.

(*iii*) **Resonance in CO<sub>2</sub> molecule.** We have said above that both carbon-oxygen bond lengths in CO<sub>2</sub> molecule are equal to 1.15 A<sup> $\circ$ </sup> (experimental value).

This value of bond length is shorter than the calculated C = O double bond length (= 1.22 A°) and larger than the calculated  $C \equiv O$  triple bond length (= 1.10 A°). In order to account for the discerpancy between the experimental and calculated values of bond length, it has been suggested that the actual structure of  $CO_2$  is a resonance hybrid of the following contributing structures :

Structure (A) is covalent while structures (B) and (C) are ionic structures. It is due to resonance that the experimentally determined value of carbon-oxygen bond lengths (= 1.15 A°) is in between that of C = O double bond (= 1.22 A°) and C = O triple bond (= 1.10 A°). The dipoles of structure (B) and (C) are equal and act in opposite directions so that the resultant dipole moment of the actual structure become zero. Observed dipole moment of  $CO_2$  molecule is also equal to zero. Thus it can be concluded that structure (B) and (C) make equal and opposite contributions to the overall structure of this molecule. The shortening of the carbon-oxygen bond lengths mentioned above is due to the stabilisation acquired through resonance.

(*iv*) To calculate bond order (B.O.) of  $CO_2$  molecule.  $CO_2$  shows resonance and it has three resonating structure given below :

Thus :

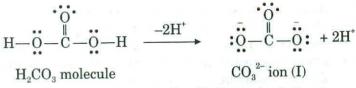
Total number of bonds between C and  $O_a$  atoms B.O. of  $CO_2 = \frac{\text{in all the three resonating structures}}{\text{Total number of resonating structures}}$  $= \frac{2+1+3}{3} = \frac{6}{3} = 2$ 

### 3. Structure of Carbonate Ion, CO<sub>3</sub><sup>2-</sup> ion.

Since O-atom is more electronegative than C-atom, the two negative (–) charges on  $CO_3^{2-}$  ion are present on two O-atoms and not on C-atoms. Thus  $CO_3^{2-}$  ion can be represented by the electron dot structure given below.

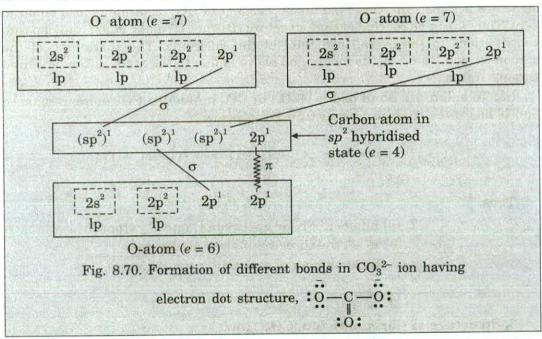
$$\begin{array}{c}
 : \overset{8}{_{0}}: \\
 : \overset{1}{_{0}} & \overset{1}{_{0}} & \overset{1}{_{0}} \\
 : \overset{2}{_{0}} & \overset{2}{_{0}} & \overset{2}{_{0}} & \overset{2}{_{0}} \\
 : \overset{2}{_{0}} & \overset{2}{_{0}} & \overset{2}{_{0}} & \overset{2}{_{0}} & \overset{2}{_{0}} & \overset{2}{_{0}} \\
 : \overset{2}{_{0}} & \overset{2}{$$

Since carbonic acid  $(H_2CO_3)$  is the parental acid of  $CO_3^{2-}$  ion, the structure of  $CO_3^{2-}$  ion can also be obtained by removing two H-atoms from two O-H groups attached directly with the central C-atoms in  $H_2CO_3$  molecule  $(H_2CO_3$  is a dibasic acid).

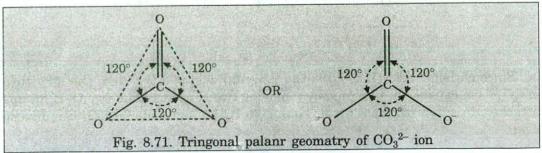


**Characteristic properties** (*i*) **Octect of electrons**. Each of the four atoms present in  $CO_3^{2-}$  ion has an octet of electrons in its respective valence-shell.

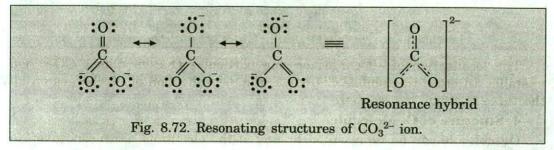
(ii)  $sp^2$  hybridisation of C-atom. The electron dot structure of  $CO_3^{2-}$  ion given above shows that since the central C-atom is surrounded by *three*  $\sigma$ -*bps* and no lp of electrons, this atom in its excited state is  $sp^2$  hybridised as shown in Fig. 8.70 The formation of different bonds in  $CO_3^{2-}$  ion is shown in the same Figure. It is evident from  $sp^2$  hybridisation scheme shown in Fig. 8.70 that one 2p orbital of C-atom remains unhybridised and contains one electron. This orbital is used to form C-O  $\pi$  bond. Obviously this  $\pi$ -bond is a  $(p\pi-p\pi)$  bond.



(*iii*) **Coplanar trigonal geometry.** Due to  $sp^2$  hybridisation and absence of lp of electrons on C-atom,  $CO_3^{2-}$  ion has coplanar tringonal geometry with OCO bond angle equal to 120°. Trignale planar geometry of  $CO_3^{2-}$  ion is shown in Fig. 8.71.



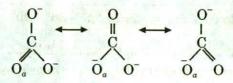
(*iv*) **Resonance in CO\_3^{2^-} ion**. X-ray examination of  $CO_3^{2^-}$  ion has indicated that all the three carbon-oxygen bonds in  $CO_3^{2^-}$  ion are of the same length (= 1.31 A°). This value is neither equal to the calculated value of C — O single bond length (= 1.43 A°) nor equal to C = O double bond length (= 1.22 A°). This value is inbetween the C — O single bond and C = O double bond lengths. In order to account for the discrepency between exprimental value (= 1.31 A°) and calculated values (= 1.43 A° and 1.22 A°) of carbon-oxygen bond lengths, it has been suggested that the true structure of  $CO_3^{2^-}$  ion is not that shown in Fig. 6.71, but it is a resonance hybrid of the resonating structure shown in Fig. 8.72.



The dotted lines shown in the resonance hybrid indicates that  $\pi$ -electron cloud in the ion is not localised between C-atom and any particular O-atom. Instead, it is spread over all the three carbon-oxygen bonds. It is due to the delocalisation of  $\pi$ -electron cloud that all the three carbon-oxygen bond lengths in  $CO_3^{2-}$  ion are equal.

(v) To Calculate bond order (B.O.) of  $CO_3^{2-}$  ion. We know that B.O of an ion showing resonance is given by :

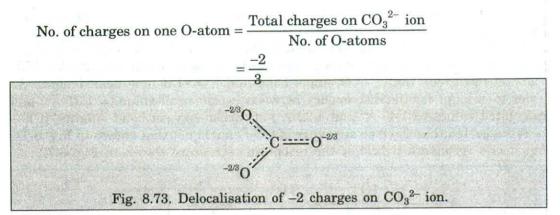
Now  $CO_3^{2-}$  ion has the following three resonanting structures.



Total number of bonds between C and  $O_a$  atoms  $\therefore$  B.O. of  $CO_3^{2-}$  ion =  $\frac{\text{in all the three resonating structures}}{\text{Total number of resonating structures}}$ =  $\frac{2+1+1}{3} = \frac{4}{3} = 1.33$ 

(vi) **Delocalisation of – 2 charges.** The two negative charges on  $CO_3^{2-}$  ion are not localised on any particular two O-atoms. Instead, these are spread over all the three O-atoms. Thus each O-atom can be regarted as having a charge equal to -2/3 as shown below. (Also see Fig. 6.73).

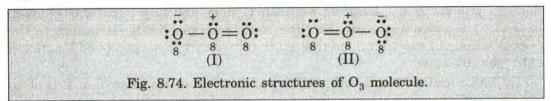
it fal and the



The localisation of -2 chrges on one particular O-atom makes  $CO_3^{2-}$  ion unstable. In order to stabilise  $CO_3^{2-}$  ion, the delocalisation of -2 charges on all the three O-atoms is essential.

## 4. Stucture of O<sub>3</sub> Molecule.

 $O_3$  molecule can be represented by any of the electronic sturucers given in Fig. 8.74.

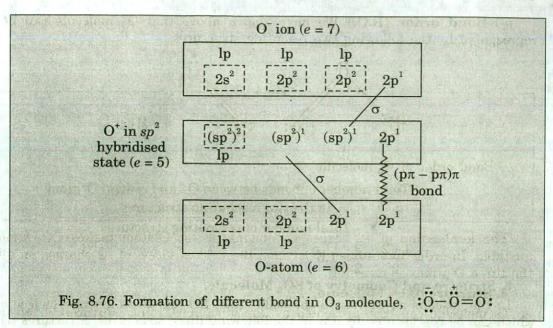


(i) Octet rule. Each of the three O-atoms in  $O_3$  molecule is surrounded by an octet of electrons. Thus  $O_3$  molecule obeys octet rule.

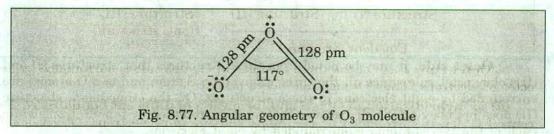
(*ii*)  $sp^2$  hybridisation of O<sup>+</sup> ion and formation of different bonds. Since the central O<sup>+</sup> ion is surrounded by two  $\sigma$ -bps and one lp of electrons, O<sup>+</sup> ion is  $sp^2$  hybridised as shown in Fig. 8.75.

O-atom $(2s^22p^4)$	$2s^2$ $2p^2$ $2p^1$ $2p^1$	and the second secon
$O^* ion (2s^2 2p^3) \dots$	$2s^2$ $2p^1$ $2p^1$ $2p^1$ $2p^1$	
$O^{+}$ ion in $sp^{2}$ }	$\underbrace{(sp^2)^2 (sp^2)^1 (sp^2)^1}_{\text{Three sp}^2 \text{ hybrid}}$	2p <sup>1</sup> Unhybridised 2p orbital
Fig. 8.75 $sp^2$ hybridisation of	O <sup>+</sup> ion in O <sub>3</sub> molecule	(: <u>ö</u> =ö:)

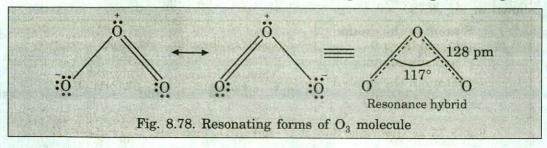
Formation of  $(O^+ - O)$  and  $(O^+ - O^-)$   $\sigma$ -bonds and  $(p\pi - p\pi) \pi$  bond in  $O_3$  molecule has been shown in Fig. 8.76.



(*iii*) Angular geometry of  $O_3$  molecule. Due to  $sp^2$  hybridisation and presence of one lp of electrons on O<sup>+</sup> atom,  $O_3$  molecule has angular geometry with bond lengths equal to 128pm. (See Fig.10.7)



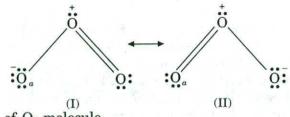
(*iv*) **Resonance.** In  $O_3$  molecule, since both oxygen-oxygen bond lengthes are the same (= 128 pm) and this distance lies in between single O – O bond distance (= 148 pm) and double O = O bond distance (= 110 pm), the true sturcture of  $O_3$  molecule is a resonance hybride of the two resonating structures given in Fig.8.78.



The following resonating structures can also be written for  $O_3$  molecule.

:ö↔ö=ö: ↔ :ö=ö→ö:

(v) **Bond order (B.O.)** We have shown above that  $O_3$  molecule can be represented by the following two resonting structures.

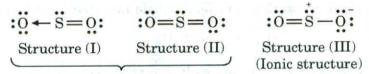


 $\therefore$  Bond order of O<sub>3</sub> molecule

Total number of bonds between  $O_{\alpha}$  and central O<sup>+</sup>atom  $= \frac{\text{in the two resonating structures}}{\text{Total number of resonating structures}}$   $= \frac{1+2}{2} = \frac{3}{2} = 1.5$ 

#### 5. Structre and Geometry of SO<sub>2</sub> Molecule.

In the gaseous as well as in the soild state,  $SO_2$  exists as discrete molecule which can be represented by any of the following three structures. Structures (I) and (II) are *covalent structures* while structure (III) is an *ionic structure*.



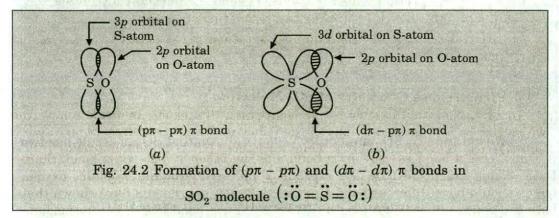
## **Covalent structures**

(i) Octet rule. It may be noted from these structures that structures (I) and (III) obey octet rule, since all the three atoms (one S-atom and two O-atoms) are surrounded by eight electrons in these structures. On the other hand, structure (II) does not obey octet rule bacause S-atom is surrounded by ten electrons while each of the two O-atoms is surrounded by eight electrons.

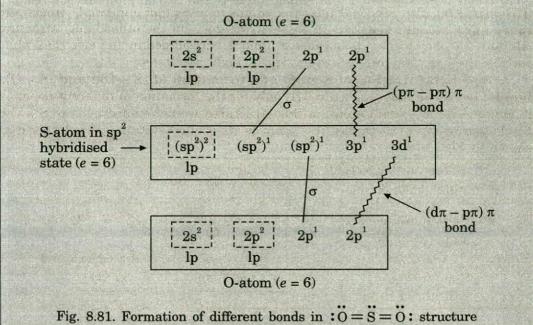
(*ii*)  $sp^2$  hybridisation of S-atom and formation of  $(S - O)\sigma$  and  $(S - O)\pi$ bonds. Let us consider structure (II) only for the formation of different bonds in it. Since S-atom (central atom) in this structured is surrounded by two  $(S - O)\sigma$ bonds and one lp of electrons, this atom in its excited state is  $sp^2$  hybridised as shown in Fig. 8.79.

	n in the ground $(3s^23p^43d^0)$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$
	in the excited $(3s^23p^33d^1)$	$\left. \begin{array}{cccccccccccccccccccccccccccccccccccc$
	n in $sp^2$	$\left\{ (sp^{2})^{2} (sp^{2})^{1} (sp^{2})^{1} \underbrace{3p^{1}}_{3p^{1}} \underbrace{3d^{1}}_{3d^{1}} \right\}$
hybridised state J	Three sp <sup>2</sup> hybrid Two unhybridised orbitals atomic orbitals	

Each of the two  $(S - O)\sigma$  bonds is obtained by end-to-end overlap (axial or liner overlop) between half-filled  $sp^2$  hybrid orbital on S-atom and half-filled 2p orbital on O-atom  $(O = 2s^2 2p^2 2p^1 2p^1)$ . Thus each  $(S - O)\sigma$  bond is  $[sp^2(S) - 2p(O)]\sigma$  bond. One of the two  $(S - O)\pi$  bonds results by the side-to-side overlap (lateral overlap) between half-filled 3p orbital on S-atom and half-filled 2p orbital on O-atom as shown in Fig. 6.80(a). Thus this  $\pi$  bond is a  $[3p(S) - 2p(O)]\pi$  bond, which is called  $(p\pi - p\pi)\pi$  bond. Other  $(S - O)\pi$  bond is obtained by the side-to-side overlap (lateral overlap) between half-filled 3d orbital on S-atom and half-filled 2p orbital on O-atom as shown in Fig. 8.80(a). Thus this  $\pi$  bond is obtained by the side-to-side overlap (lateral overlap) between half-filled 3d orbital on S-atom and half-filled 2p orbital on O-atom as shown in Fig. 8.80(b). Thus this  $(S - O)\pi$  bond is a  $[3d(S) - 2p(O)]\pi$  bond which is called  $(d\pi - p\pi)\pi$ .



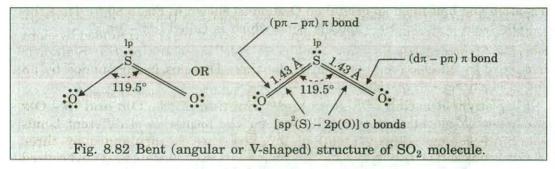
Formation of both  $(S - O)\sigma$  and both  $(S - O)\pi$  bonds in structure (II) of  $SO_2$  molecule has been shown in simplified manner in Fig. 8.81.



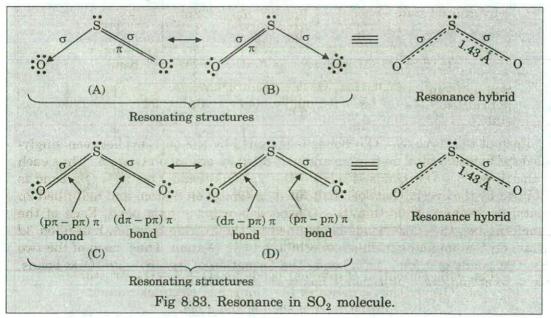
of SO<sub>2</sub> molecule. e indicates the number of electrons present in the valence shell of the atom.

#### Modern Inorganic Chemistry

(*iii*) Angular shape of SO<sub>2</sub> molecule and OSO bond angle. It is due to the presence of one lp of electrons in one of the three  $sp^2$  hybrid orbitals on S-atom that SO<sub>2</sub> molecule does not have the expected trigonal planer shape corresponding to  $sp^2$  hybridisation of S-atom and OSO bond angle is also not equal to the expected angle of 120° for trigonal planar geometry. Rather, its expected trigonal shape gets distorted and becomes *bent* or *angular* (V-shape). Since (lp - bp) repulsion is greater than (bp - bp) replusion, OSO bond angle gets sligthly reduced from 120° to 119.5° [See Fig. 8.82]

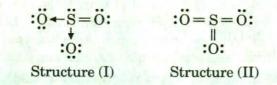


(*iv*) **Resonance in SO**<sub>2</sub> **molecule.** We have shown that SO<sub>2</sub> molecule has two  $\pi$  bonds. One  $\pi$  bond is  $(p\pi - p\pi)\pi$  bond and the other is  $(p\pi - d\pi)\pi$  bond. Since these bonds are formed by the overlap of different orbitals, sulphur—oxygen bonds should have different bond lengths. However, expriments have shown that both the bonds are of equal length (= 1.43 A°). Each bond length is intermediate between the calculated value of S – O single bond length and S = O double bond length. In order to explain the equivalence of both sulphur—oxygen bond lengthe in SO<sub>2</sub> it has been suggested that equal length of the two sulphur—oxygen bonds is because of the resonance between two resonating structures (A) and (B) or (C) and (D) shown in Fig. 8.83.



## 6. Structure of SO3 molecule in the Gaseous State.

In the gaseous state  $SO_3$  molecule exists as a monomeric molecule,  $SO_3$ . This molecule can have any of the following two structures :

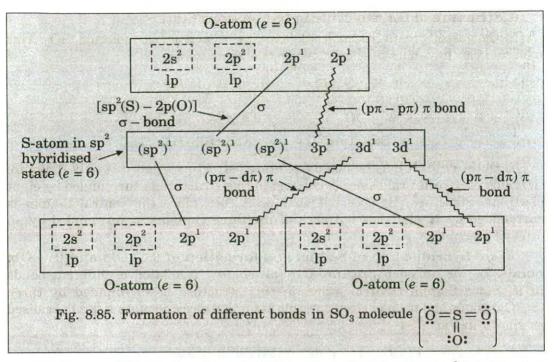


(i) **Octet rule.** It may be noted from these structures that it is only structure (I) which obeys octet rule since each atom in this structure is surrounded by eight electrons. Structure (II) does not obey octet rule, since the central S-atom is surrounded by 12 electrons but each of the three O-atoms is surrounded by an octet of electrons

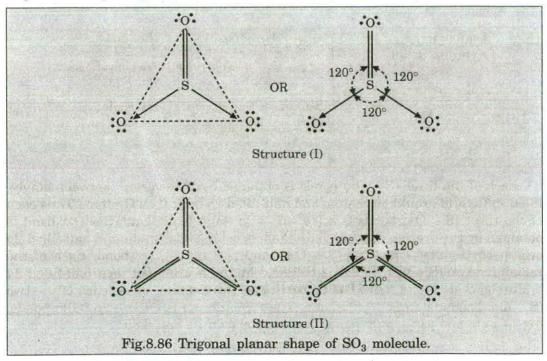
(ii)  $sp^2$  hybridisation of S-atom and formation of  $(S - O)\sigma$  and  $(S - O)\pi$ bonds. Let us consider structure (II) only for the formation of different bonds in it. Since S-atom (central atom) in this structure is surrounded by three  $(S - O)\sigma$  bonds and no lp of electrons, this atom in its excited state is  $sp^2$  hybridised as shown in Fig. 8.84

S-atom in the ground state $(3s^23p^43d^0)$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$^{1}$ $3d^{0}$ $3d^{0}$
S-atom in the 2nd excited state	$\left.\right\}  3s^1  3p^1  3p^1  3p$	$^{1}$ $3d^{1}$ $3d^{1}$
S-atom in <i>sp</i> <sup>2</sup> hybridised state	$\left. \begin{array}{c} \underbrace{(sp^2)^1 (sp^2)^1 (sp^2)^1}_{\text{Three sp}^2 \text{ hybrid}} \\ \text{orbitals} \end{array} \right.$	$\underbrace{3p^1 3d^1 3d^1}_{\text{Three unhybridised}}$
	bridisation of S-atom in ng :Ö=S=Ö: structur	SO3 molecule

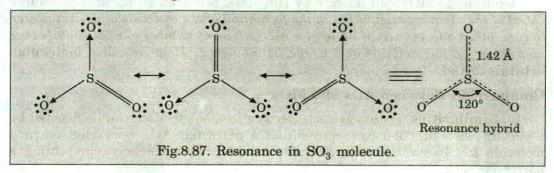
Each of the three  $(S - O)\sigma$  bonds is obtained by the overlap between singlyfilled  $sp^2$  hybrid orbital on S-atom and half-filled 2p orbital on O-atom.. Thus each of the three  $(S - O)\sigma$  bonds is a  $[sp^2 (S) - 2p (O)]\sigma$  bond. One  $(S - O)\pi$  bond is obtained by the overlap between half-filled 3p orbital on S-atom and half-filled 2porbital on O-atom. Thus this  $(S - O)\pi$  bond is a  $(p\pi - p\pi)\pi$  bond. Each of the remaining two  $(S - O)\pi$  bonds is obtained by the overlap between half-filled 3dorbital on S-atom and half-filled 2p orbital on two O-atom. Thus each of the two  $(S - O)\pi$  bonds is a  $(d\pi - p\pi)\pi$  bond. The formation of  $[sp^2 (S) - 2p (O)]\sigma$  bonds,  $(p\pi - p\pi)\pi$  and  $(d\pi - p\pi)\pi$  bonds has been shown in Fig. 8.85.



(*iii*) Shape of SO<sub>3</sub> molecule and OSO bond angle. It is due to  $sp^2$  hybridisation of the central S-atom and absence of any lone pair of electrons on the central S-atom that SO<sub>3</sub> molecule has the expected *trigonal planar geometry* (See Fig. 8.86. Each of the three OSO bond angles is equal to 120° which is the expected angle for a *trigonal planar geometry*.

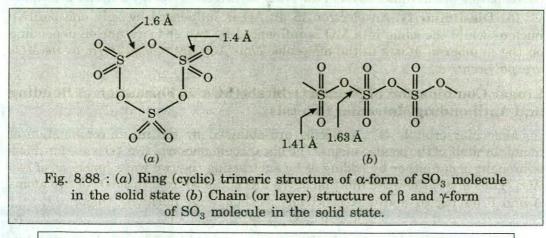


(iv) **Resonance in SO**<sub>3</sub>. We have already shown that SO<sub>3</sub> molecule has three  $\pi$  bonds. One  $\pi$  bond is  $(p\pi - p\pi)\pi$  bond and the other two  $\pi$ -bonds are  $(p\pi - d\pi)\pi$  bonds. Length of the two  $(p\pi - d\pi)\pi$  bonds should be the same but different from that of  $(p\pi - p\pi)\pi$  bond. Expriments have, however, shown that all the three sulphur-oxygen bonds in SO<sub>3</sub> are of equal length (= 1.42 A°). Each bond length is intermediate between the calculated value of S – O single bond length and S = O double bond length. In order to explain the equivalence of all the three sulphur-oxygen bond lengths in SO<sub>3</sub>, it has been suggested that equal lengths of the bonds is because of resonance between the three resonating structures (A), (B) and (C) shown in Fig. 8.87.



#### 7. Structure of SO<sub>3</sub> Molecule in the Solid State.

 $\alpha$ -form of SO<sub>3</sub> solid molecule gets polymerised and gives a trimer, (SiO<sub>3</sub>)<sub>3</sub>. Which has a ring (cyclic) structure shown at (a) of Fig. 6.88. On the other hand,  $\beta$  and  $\gamma$ -forms of solid SO<sub>3</sub> have linear layer (or chain) structure shown at (b) of Fig. 8.88. This structure consists of a number of SO<sub>3</sub> chains linked together. These chains are produced when many SO<sub>4</sub> tetrahedrons get linked together by the sharing of O-atom.



# Molecular Orbital Theory (MOT) of Covalent Bond: Hund-Mullikan Theory

We have seen that the atomic orbital theory (Valence Bond Theory, VBT) of covalent bond is based on the assumption that the formation of a bond between the atoms of a given molecule involves the overlapping of the atomic orbitals which are half-filled. These half-filled orbitals (called bonding orbitals) merge (*i.e.* overlap or mix) into one another and give a bond (or an orbital) which is responsible for the stability of the resulted molecule. All other orbitals which are completely-filled do not participate in the process of overlapping and hence do not contribute to bond formation. In other words all the completely-filled orbitals maintain their individual indentity. However, this seems to be an exaggeration because the nucleus of an approaching atom is bound to affect the electron- waves of nearly all orbitals. Apart from this, VBT fails to explain some of the properties of some molecules like  $O_2$ .

According to MOT, put forward by Hund and Mullikan all the atomic orbitals (AOs) of the atoms participating in the formation of the molecule approach nearer to each other and get mixed up to give an equivalent number of new orbitals that now belong to the molecule as a whole. These new orbitals are called **molecular** orbitals (MOs).

## **Comparison Between AOs and MOs**

(a) **Similarities** (i) Just as each electron in a single atom can be denoted by a certain wave-function  $(\psi)$  representing a particular AO, every electron in a molecule can like wise be denoted by a similar wave function representing a particular MO.

(ii) Like an AO, a MO can accomodate a maximum of two electrons which should have opposite spins. In other words, MOs, like AOs, obey Paulie's exclusion principle and Hund's rule.

(iii) Like AOs, various MOs of a molecule have different energies and different shapes.

(*iv*) Electrons in the molecule (except those residing in the inner-shells of the participating atoms) enter MOs in the order of increasing energy (Aufbau principle).

(b) **Dissimilarity.** An electron in an AO is influenced by only one positive nucleus while the same in a MO is influenced by two or more nuclei, depending on the number of atoms in the molecule. *Thus AOs are mono-centric while MOs are poly-centric*.

## Linear Combination of Atomic Orbitals (LCAO): Formation of Bonding and Antibonding Molecular Orbitals

Molecular orbitals of a molecule are obtained by the linear combination of atomic orbitals of the bonded atoms. The linear combination of two AO wave functions is brought about either by adding or by subtracting the two wave functions of two AOs. Thus if  $\psi$  is the wave function of the MO obtained from two AOs of two atoms A and B having  $\psi_A$  and  $\psi_B$  respectively as their wave functions, then :

$$\Psi = \Psi_{\rm A} \pm \Psi_{\rm B}$$

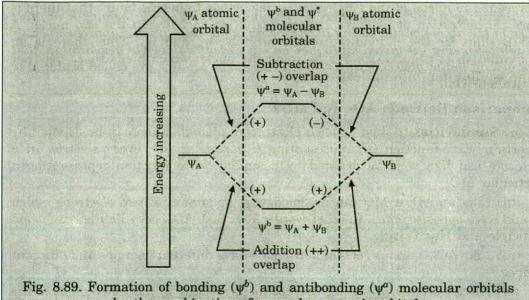
Equation (i) clearly shows that the linear combination of  $\psi_A$  and  $\psi_B$  gives two MOs. One of these is represented as  $\psi^b$  and the other as  $\psi^a$ . These are thus given by

$$\begin{split} \Psi^{b} &= \Psi_{A} + \Psi_{B} & \dots (ii) \\ \Psi^{a} &= \Psi_{A} - \Psi_{B} & \dots (iii) \end{split}$$

...(i)

and

 $\Psi^b$  has lower energy than that of either of the AOs from which it is formed. This MO thus leads to the formation of a stable molecule, AB and is, therefore, called a **bonding molecular orbital**. The other MO namely  $\Psi^a$  has higher energy than that of  $\Psi_A$  and  $\Psi_B$  and is, therefore, called an **antibonding molecular orbital** (Fig. 6.89). The superscript b used in  $\Psi^b$  indicates that the molecular orbital is bonding molecular orbital while a used in  $\Psi^a$  indicates that the molecular orbital is antibonding. The number of molecular orbitals is always equal to the number of atomic orbitals involved in the formation of molecular orbitals.



by the combination of  $\psi_A$  and  $\psi_B$  atomic orbital.

The plus sign in equation (*ii*) indicates that the  $\Psi^b$  MO is obtained when the regions of AOs marked with positive sign overlap with each other. In this case it is said that the two AOs have been *added*. On the other hand in equation (*iii*) negative sign indicates that  $\Psi^a$  is obtained when the region of positive sign of one AO (say of  $\Psi_A$ ) overlaps with the region of negative sign of the other AO (say of  $\Psi_B$ ). In this case we say that the two AOs have been *subtracted*.

# Electronic Charge Density of Bonding $(\Psi^b)$ and Anti-bonding $(\Psi^a)$ Molecular Orbitals

In order to understand the significance of bonding and anti-bonding molecular orbitals in terms of wave functions it is necessary to know the electronic charge distribution of these orbitals.

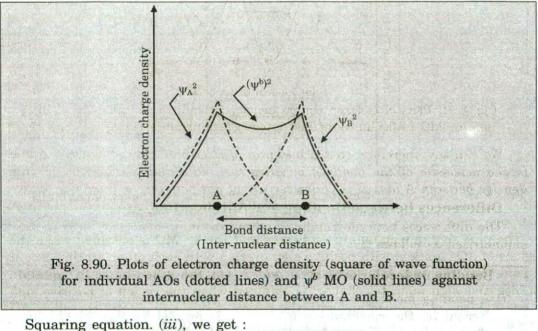
Squaring the equation (ii) we get :

$$(\psi^{b})^{2} = \psi_{A}^{2} + \psi_{B}^{2} + 2\psi_{A}\psi_{B}$$

...(iv)

The terms  $\psi_A^2$  and  $\psi_B^2$  indicate the electronic charge densities of the wave functions  $\psi_A$  and  $\psi_B$  of the isolated atoms A and B while the term  $(\psi^b)^2$  indicates that of the wave function  $\psi^b$  of the bonding molecular orbital. Obviously greater the value of  $(\psi^b)^2$ , greater is the charge density between the two atomic nuclei and stronger is the bond between them. It may be seen from equation (iv) that  $(\psi^b)^2 >$  $(\psi_A^2 + \psi_B^2)$  by a term  $2\psi_A\psi_B$ . This term results from the *interaction* or *overlap* of atomic orbitals. Thus larger is the overlap of atomic orbitals, greater is the charge density between the nuclei and more stable is the bond formed between A and B.

Fig. 8.90. contains the plot of electron charge density for bonding molecular orbital,  $(\psi^b)^2$  and for individual atomic orbitals  $(\psi_A^2 \text{ and } \psi_B^2)$  against the internuclear distance (*i.e.* the distance between the two nuclei A and B).  $(\psi^b)^2$  has been shown by solid lines and  $\psi_A^2$  and  $\psi_B^2$  by dotted lines. The points A and B represent the nuclei of the two atoms. It is obvious from this figure that there is more concentration of negative charge in the region between the two nuclei, A and B than for the individual atomic orbitals,  $\psi_A$  and  $\psi_B$ . Thus there is an accumulation of negative charge between the nuclei which holds these together at an equilibrium internuclear distance.



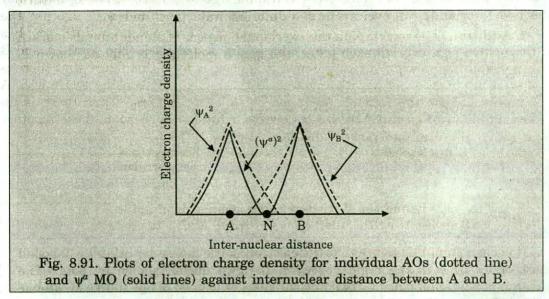
$$(\psi^{a})^{2} = \Psi_{A}^{2} + \Psi_{B}^{2} - 2\Psi_{A}\Psi_{B}$$

...(v)

It may be seen from this equation that  $(\Psi^a)^2 < (\Psi_A^2 + \Psi_B^2)$  by a term  $2\Psi_A\Psi_B$ . This means that in antibonding molecular orbital there is less charge density between the interacting atoms than there would be between the non-interacting atoms. Thus the energy of this antibonding molecular orbital is greater than the sum of the energies of the two interacting atoms A and B and the resulting bond formed between A and B is less stable.

In Fig. 8.91  $(\Psi^a)^2$  is shown by the solid line while  $\Psi_A^2$  and  $\Psi_B^2$  by dotted line. Plot of  $(\Psi^{\alpha})^2$  touches the axis at midpoint N between the nuclei A and B. This point is called a node point and at this point the electron density is zero. Thus the formation of  $\Psi^a$  molecular orbital decreases the electron charge density in the region between the two nuclei A and B over that of the individual atoms. Negative charge is withdrawn from the region between the nuclei and is concentrated

round the nucleus. This makes the electrons repel each other in the region between A and B. Thus we can say that in  $\Psi^a$  molecular orbital an electron spends half of its time on each of the individual atoms and consequently is never found in the region between A and B *i.e.* the probability of finding the electron in the region between A and B is decreased.



We can say, therefore, that a build-up of electronic charge between A and B is characteristic of the bonding or attractive state and a depletion of charge density between A and B is characteristic of antibonding or repulsive state.

Differences Between Bonding and Anti-bonding Molecular Orbitals.

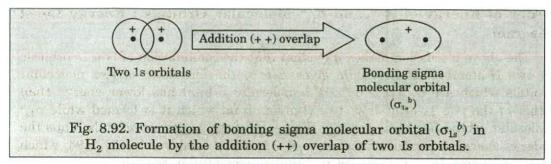
The differences between bonding and anti-bonding molecular orbitals can be summarised as follows :

Bonding molecular orbital	Anti-bonding molecular orbital
<ul> <li>(i) A bonding molecular orbital is</li></ul>	(i) An anti-bonding molecular orbital
formed by the combination of	is formed by the combination of
electron-waves of the same sign,	electron waves of the opposite
<i>i.e.</i> by the addition-overlap of	sign, <i>i.e.</i> by the subtraction-
atomic orbitals.	overlap of atomic orbitals.
( <i>ii</i> ) Bonding molecular orbital	( <i>ii</i> ) Anti-bonding molecular orbital
possesses <i>lower</i> energy than the	possesses higher energy than the
atomic orbitals from which it is	atomic orbitals from which it is
formed.	formed.
( <i>iii</i> ) The electron density in between	( <i>iii</i> ) The electron density in between
the nuclei is <i>high</i> and hence the	the nuclei is low and hence the
attraction between the nuclei	repulsion between the nuclei is
is high. This explains the for-	high. This explains the non-
mation of a bond between the	formation of the bond between the
atoms.	atoms.

## Formation of Molecular Orbitals from s-Atomic Orbitals

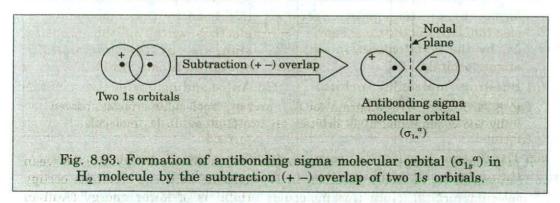
We may consider the formation of molecular orbitals obtained by the combination of two 1s orbitals on two H-atoms in  $H_2$  molecule. In this combination 1s orbital of one H-atom overlaps with the 1s orbital of the other H-atom to give *two* molecular orbitals in  $H_2$  molecule. Since the electrons have wave-like-nature, the two 1s orbitals can overlap in two different ways given below :

1. Addition (+ +) overlap. In this overlap the regions of atomic orbitals marked with positive sign overlap each other and give a molecular orbital as shown in Fig. 8.92.



It is clear from this figure that the electron in the molecular orbital will spend most of its time in the region between the two nuclei (shown by dots). The electron is now stabilished by two nuclear charges instead of one unlike an atomic orbital. The resulting molecular orbital has lower energy than either of the two 1s orbitals and hence is called bonding molecular orbital. Since the molecular orbital is symmetric to rotation about the inter-nuclear axis, *i.e.* it does not show any change of sign on rotation through 180° through the inter-nuclear axis, it is a sigma ( $\sigma$ ) molecular orbital. Thus this molecular orbital is a **bonding sigma molecular orbital** and hence is represented as  $\sigma_{1s}^{b}$ .

2. Subtraction (+ -) overlap. In this overlap the region of positive sign of one atomic orbital overlaps with the region of negative sign of the other atomic orbital and gives a molecular orbital as shown in Fig. 8.93.



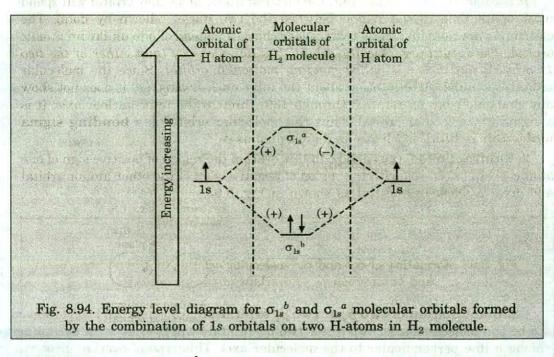
The resulting molecular orbital has zero electron density (*nodal plane*) in the region between the two nuclei (shown by dots). The electron in this molecular

orbital is concentrated in region away from each of the nuclei. The resulting molecular orbital is of higher energy than either of the two 1s-orbitals and hence is called antibonding molecular orbital. Since this molecular orbital is also symmetric to rotation about the inter-nuclear axis, it is also a sigma ( $\sigma$ ) molecular orbital. Thus this molecular orbital is an **antibonding sigma molecular orbital** and is, therefore, represented as  $\sigma_{1s}{}^{a}$ .

Similarly the combination of two 2s orbitals gives  $\sigma_{2s}^{\ b}$  and  $\sigma_{2s}^{\ a}$  molecular orbitals. Their formation can be shown in the same way as that of  $\sigma_{1s}^{\ b}$  and  $\sigma_{1s}^{\ a}$  molecular orbitals has been shown in Figures 8.92. and 8.93.

# Order of Energy of $\sigma_{1s}{}^{b}$ and $\sigma_{1s}{}^{a}$ Molecular Orbitals : Energy Level Diagram

The above discussion makes it evident that the combination of two 1s orbitals on two H-atoms of H<sub>2</sub> molecule gives rise to the formation of two molecular orbitals which are  $\sigma_{1s}{}^{b}$  and  $\sigma_{1s}{}^{a}$ .  $\sigma_{1s}{}^{b}$  molecular orbital has lower energy than either of the two 1s orbitals of two H-atoms from which it is formed while  $\sigma_{1s}{}^{a}$ molecular orbital has higher energy than each of the 1s atomic orbitals. Thus the order of energy of various orbitals is  $\sigma_{1s}{}^{b} < 1s < \sigma_{1s}{}^{a}$  as shown in Fig. 8.94. which is called energy level diagram of  $\sigma_{1s}{}^{b}$  and  $\sigma_{1s}{}^{a}$  molecular orbitals.



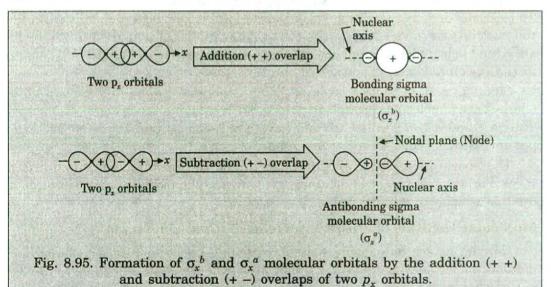
It is the lower energy  $\sigma_{1s}^{b}$  molecular orbital which makes the bonding between two H-atoms in H<sub>2</sub> molecule possible. In H<sub>2</sub> molecule both the electrons occupy  $\sigma_{1s}^{b}$  molecular orbital, since this molecular orbital is of lower energy (Aufbau principle). Thus  $\sigma_{1s}^{a}$  molecular orbital which has higher energy remains vacant.

## Formation of Molecular Orbitals from p-Atomic Orbitals

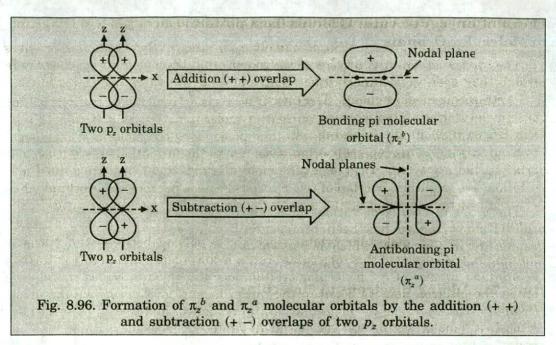
Since there are three p orbitals namely  $p_x$ ,  $p_y$  and  $p_z$ , their combination gives rise to the formation of two types of molecular orbitals, depending on the way in which they overlap with each other. The following two cases may be studied.

**1. Combination of two**  $p_x$  orbitals. If x-axis is assumed to be the axis joining the two nuclei in a molecule (*i.e.* nuclear or molecular axis, as it is called), then the combination of two  $p_x$  orbitals will take place along the molecular axis (head-to-head overlap). This type of overlap gives rise to the formation of two molecular orbitals that are symmetrical about the molecular axis and hence are  $\sigma$  molecular orbitals. + + (addition) overlap of two  $p_x$  orbitals gives  $\sigma_x^b$  molecular orbital while + - (subtraction) overlap of the same orbitals gives  $\sigma_x^a$  molecular orbital (Fig. 8.95).

In case of  $\sigma_x^{\ b}$  molecular orbital since the repulsion between the nuclei is minimum, the energy of this molecular orbital is lower than that of any of the two  $p_x$  orbitals. In case of  $\sigma_x^{\ a}$  molecular orbital since the electron waves cancel each other, the electron density between the nuclei is very low and hence the nuclei *fly apart*. The energy of  $\sigma_x^{\ a}$  molecular orbital is higher than that of  $\sigma_x^{\ b}$  molecular orbital.  $\sigma_x^{\ b}$  molecular orbital has no node while  $\sigma_x^{\ a}$  molecular orbital has one node.



2. Combination of two  $p_y$  or two  $p_z$  orbitals. Since x-axis has been assumed to be the molecular axis, two  $p_y$  (or two  $p_z$ ) orbitals will overlap with each other along a line perpendicular to the molecular axis. This type of overlap gives rise to the formation of two molecular orbitals that are not symmetrical about the molecular axis and hence are not sigma molecular orbitals. Rather such orbitals are called  $pi(\pi)$  molecular orbitals. + + (addition) overlap of, say, two  $p_z$  orbitals gives  $\pi_z^b$  molecular orbital while + - (subtraction) overlap of the same orbitals gives  $\pi_z^a$  molecular orbital (Sec Fig. 8.96).



Similarly the overlap of two  $p_y$  orbitals gives  $\pi_y^{\ b}$  and  $\pi_y^{\ a}$  molecular orbitals. The electron density in  $\pi_z^{\ b}$  or  $\pi_y^{\ b}$  molecular orbital is zero on a plane that contains the nuclear axis (nodal plane). The electron density is concentrated in the region above and below this nodal plane.  $\pi_z^{\ a}$  or  $\pi_y^{\ a}$  molecular orbital has the least energy in the region between the nuclei of the two atoms.

Since  $p_y$  and  $p_z$  atomic orbitals on an atom are degenerate (are of equal energy), the  $\pi$  molecular orbitals formed by their combination are also degenerate. Thus  $\pi_y^{\ b}$  and  $\pi_z^{\ b}$  molecular orbitals have equal energy and the same situation prevails with  $\pi_y^{\ a}$  and  $\pi_z^{\ a}$  molecular orbitals.

The above discussion makes it evident that the combination of two sets of three p orbitals on two isolated atoms gives rise to the formation of six molecular orbitals which are  $\sigma_x^{\ b}$ ,  $\sigma_x^{\ a}$ ,  $\pi_y^{\ b}$ ,  $\pi_z^{\ a}$ ,  $\pi_z^{\ b}$  and  $\pi_z^{\ a}$ .

## **Molecular Orbitals of a Homo-nuclear Diatomic Molecule**

Now let us see how many molecular orbitals are formed in a homo-nuclear diatomic molecule whose both the atoms are of the elements belonging to the 2nd period of the long form of periodic table. Obviously these molecules may be Li<sub>2</sub>, Be<sub>2</sub>, B<sub>2</sub>, C<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, F<sub>2</sub> and Ne<sub>2</sub>. Since the isolated atoms of Li<sub>2</sub> and Be<sub>2</sub> molecules contain 1s and 2s orbitals only, these orbitals, on combination, give rise to the formation of *four* molecular orbitals which are  $\sigma_{1s}^{\ b}$ ,  $\sigma_{1s}^{\ a}$ ,  $\sigma_{2s}^{\ b}$ , and  $\sigma_{2s}^{\ a}$ . In case of B<sub>2</sub>, C<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, F<sub>2</sub> and Ne<sub>2</sub> molecules, since the isolated atoms contain 1s, 2s and 2p orbitals, these orbitals, on combination, give rise to the formation of the following *ten* molecular orbitals :

$$\sigma_{1s}^{\ b}, \sigma_{1s}^{\ a}, \sigma_{2s}^{\ b}, \sigma_{2s}^{\ a}, \sigma_{x}^{\ b}, \sigma_{x}^{\ a}, \pi^{b}, \pi_{y}^{\ a}, \pi_{z}^{\ b}, \pi_{z}^{\ a}$$

# Order of Energy of Various Molecular Orbitals : Energy Level Diagram of Molecular Orbitals

The order of energy of the molecular orbitals has been determined experimentally by spectroscopic measurements. The energy of these molecular orbitals increases as we move from left to right in the following list.

$$\begin{array}{c|c} \hline & Energy \ increasing \\ \hline \sigma_{1s}^{\ b} < \sigma_{1s}^{\ a} < \sigma_{2s}^{\ b} < \sigma_{2s}^{\ a} < \pi_{y}^{\ b} = \pi_{z}^{\ b} < \sigma_{x}^{\ b} \\ < \pi_{y}^{\ a} = \pi_{z}^{\ a} < \sigma_{x}^{\ a} \end{array}$$

The order of energy of various molecular orbitals shown above has been represented graphically in Fig. 8.97. which is known as molecular orbital energy level diagram.

## Rules for Adding Electrons to Molecular Orbitals

Electrons are added to the molecular orbitals in the same way as they are added to the atomic orbitals. The rules are given below :

(i) The molecular orbitals are filled with electrons in the increasing order of their energy, *i.e.*, the molecular orbital having the lowest energy is filled up first while that with the highest energy is filled up in the end.

(ii) Hund's rule is also obeyed by the degenerate molecular orbitals. According to this rule the degenerate orbitals are first singly filled and pairing starts when more electrons are to be accommodated.

(*iii*) The maximum number of electrons that a molecular orbital can contain is two. These two electrons must have opposite spins.

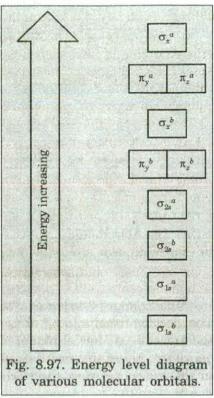
## Bond Order (B.O) or Bond Multiplicity

The electrons in the bonding molecular orbitals help in the formation of bonds while those in the antibonding molecular orbitals oppose it. Bond order (B.O) is defined as the number of covalent bonds between the two combining atoms of a molecule and is equal to one-half of the difference between the number of electrons in bonding molecular orbitals  $(n_b)$  and that in the antibonding molecular orbitals  $(n_a)$ .

Thus :

Bond Order = 
$$\frac{1}{2}(n_b - n_a)$$

In common practice, the electrons residing in the molecular orbitals formed only from the orbitals of the valence-shell are considered for determining the bond order.



## **Conditions for Effective Combination of Atomic Orbitals**

There are certain conditions which are necessary for the AOs to be able to combine effectively. These conditions are given below :

(i) The energies of the AOs combining together must be similar in magnitude or the AOs should have comparable energies. Thus in case of the formation of a homo-nuclear diatomic molecule of  $A_2$  type, the 1s AO of one atom A will not combine with the 2s AO of the other atom since their energies are not equal. Similarly since the energy difference between 2s- and 2p- AOs is too great, they will also not combine.

But in case of the formation of hetero-nuclear diatomic molecule of AB type, such combinations may be expected.

(*ii*) The charge clouds of AOs must overlap one another as much as possible, if they are going to combine together to form the MOs. This condition is often referred to as the *principal of maximum overlap*.

(*iii*) The AOs should have the same symmetry about the molecular axis. This condition is known as symmetry condition for the combination of AOs.

On the basis of this symmetry condition it is noted that some of the AOs which have comparable energies do overlap, but cannot combine to give MOs. Thus MOs cannot be formed by the overlap of an *s*-atomic orbital of atom A and one *p*-atomic orbital of atom B perpendicular to the molecular axis. The cause of non-formation of MOs is that the symmetry of *s*-orbital is not the same as that of *p*-orbital. Alternatively it can be said that + + overlap is neutralised by the + - overlap or in other words the + - overlap cancels the bonding contribution from the + + overlap.

## **Molecular Orbital Configuration of Homo-nuclear Diatomic Species**

For diatomic species (homo-nuclear and hetero-nuclear both) obtained from atoms having more than one electronic shells, the atomic orbitals of the innershells are deeply seated and the molecular orbitals formed by the overlap of these orbitals do not affect the bonding and hence can be omitted. The electrons in these molecular orbitals are called *non-bonding electrons* and the molecular orbitals containing these electrons are known as *non-bonding molecular orbitals*. Thus when we are considing a diatomic molecule, we consider only those molecular orbitals that are formed by the overlap of atomic orbitals belonging to the valenceshell only.

1.  $\mathbf{H}_2$  molecule  $(\mathbf{H}\rightarrow \mathbf{ls}^1, e = 1)$ . We have already said that the combination of two 1s orbitals on two H-atoms in  $\mathbf{H}_2$  molecule gives rise to the formation of  $\sigma_{1s}{}^b$  and  $\sigma_{1s}{}^a$  molecular orbitals whose energies are in the order :  $\sigma_{1s}{}^b < \sigma_{1s}{}^a$ . Both the electrons go to the lower energy  $\sigma_{1s}{}^b$  molecular orbital and hence  $\sigma_{1s}{}^a$  molecular remains vaccant. Thus the molecular orbital configuration of  $\mathbf{H}_2$  molecule is  $(\sigma_{1s}{}^b)^2$  $(\sigma_{1s}{}^a)^0$ , showing that  $n_a = 2$ ,  $n_b = 0$ , and hence :

Bond order  $=\frac{2}{2}=1$ 

Bond order equal to 1 implies that two H-atoms in  $H_2$  molecule are bonded together by one  $\sigma$  bond (H—H).

2. Hydrogen molecule ion,  $H_2^+$  ( $H \rightarrow ls^1$ ,  $H^+ \rightarrow 1s^0$ , e = 1). This ion has one hydrogen atom and one  $H^+$  ion linked together. Each of these has 1s-atomic orbital. Using the LCAO method the two 1s-orbitals will combine together to give  $\sigma_{1s}{}^b$  and  $\sigma_{1s}{}^a$  molecular orbitals.  $H_2^+$  ion has only one electron which occupies lower energy  $\sigma_{1s}{}^b$  molecular orbital and hence  $\sigma_{1s}{}^a$  molecular orbital remains vaccant. Thus the molecular orbital configuration of  $H_2^+$  ion is  $(\sigma_{1s}{}^b)^1$   $(\sigma_{1s}{}^a)^0$ , showing that  $n_b = 1$ ,  $n_a = 0$ , and hence bond order of  $H^+$  ion is one-half  $(\frac{1}{2}\sigma)$  of a normal covalent bond. Low bond order of  $H_2^+$  ion explains its low bond dissociation energy (= 255.28 KJ. mole<sup>-1</sup>) and large bond length (= 1.06 A°)

**3.** He<sub>2</sub> molecule (He $\rightarrow$ 1s<sup>2</sup>, e = 4). He atom has the configuration 1s<sup>2</sup>. For the formation of He<sub>2</sub> molecule  $\sigma_{1s}{}^{b}$  and  $\sigma_{1s}{}^{a}$  molecular orbitals are required. Four electrons (two contributed by each He atom) are to be accommodated in these molecular orbitals. Thus the molecular orbital configuration of He<sub>2</sub> molecule is  $(\sigma_{1s}{}^{b})^{2} (\sigma_{1s}{}^{a})^{2}$ , showing that  $n_{b} = 2$ ,  $n_{a} = 2$ , and hence bond order = (2-2)/2 = 0, Bond order equal to zero implies that He<sub>2</sub> molecule does not exist.

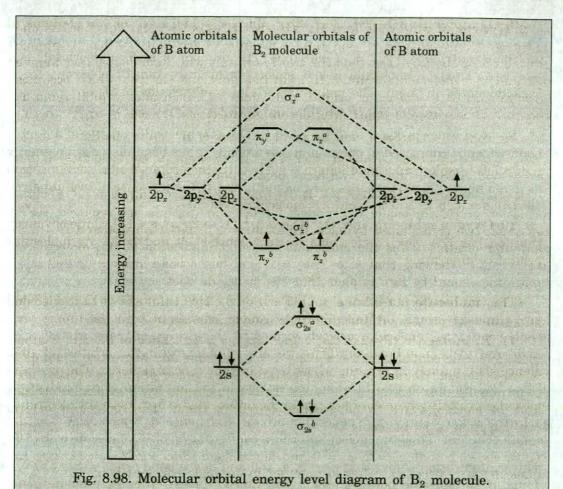
4. Li<sub>2</sub> molecule  $(Li \rightarrow 2s^1, e = 2)$ . Each of the two Li atoms of Li<sub>2</sub> molecule has 1s and 2s atomic orbitals. Since 1s-atomic orbitals of both the atoms are deeply seated, the molecular orbitals formed by the overlap of these orbitals are considered to be non-bonding. Thus we are left only with the orbitals of the valence-shell namely 2s orbitals whose overlap should be considered. The overlap of two 2s orbitals on two Li atoms gives rise to the formation of  $\sigma_{2s}{}^{b}$  and  $\sigma_{2s}{}^{a}$ molecular orbitals whose energies are in the order :  $\sigma_{2s}{}^{b} < \sigma_{2s}{}^{a}$ . Both the electrons go to the lower energy  $\sigma_{2s}{}^{b}$  molecular orbital and hence  $\sigma_{2s}{}^{a}$  molecule is  $(\sigma_{2s}{}^{b})^{2}$  $(\sigma_{2s}{}^{a})^{0}$ , showing that  $n_{b} = 2$ ,  $n_{a} = 0$  and hence bond order = 2/2 = 1, *i.e.* two Li atoms in Li<sub>2</sub> molecule are linked together by a single covalent bond.

**5.** Be<sub>2</sub> molecule (Be $\rightarrow$ 2s<sup>2</sup>, e =4). Valence-shell of Be atom has 2s orbital. Two 2s orbitals on two Be atoms in Be<sub>2</sub> molecule overlap each other and form  $\sigma_{2s}^{b}$  and  $\sigma_{2s}^{a}$  molecular orbitals. Both the molecular orbitals are filled with four electrons. Thus the molecular orbital configuration of Be<sub>2</sub> molecule is  $(\sigma_{2s}^{b})^2 (\sigma_{2s}^{a})^2$ , showing that  $n_b = 2$ ,  $n_a = 2$  and hence bond order = (2 - 2)/2 = 0, *i.e.* Be<sub>2</sub> molecule does not exist.

**6.**  $B_2$  molecule ( $B \rightarrow 2s^2$ ,  $2p_x^1$ ,  $2p_y^0$ ,  $2p_z^0$ , e = 6). It is the first element in which *p*-orbital starts. Its valence-shell configuration is  $2s^2$ ,  $2p_x^1$ ,  $2p_y^0$ ,  $2p_z^0$ , with three electrons. Thus  $B_2$  molecule has in all 3 + 3 = 6 electrons and its molecular orbital configuration is :

 $(\sigma_{2s}{}^{b})^{2}, (\sigma_{2s}{}^{a})^{2}, (\pi_{v}{}^{b})^{1} = (\pi_{z}{}^{b})^{1}$  (See Fig. 8.98)

Bond order of  $B_2$  molecule in equal to  $\frac{1}{2}$  (4-2) = 1 which shows that  $B_2$  molecule is formed by a weak  $\pi$ -bond and has two unpaired electrons in  $\pi$ -molecular orbitals. This has been verified by experiments. Due to the presence of two unpaired electrons,  $B_2$  molecule is *paramagnetic*.



7.  $C_2$  molecule  $(C \rightarrow 2s^2, 2p_x^{1}, 2p_y^{1}, 2p_z^{0}, e = 8)$ .  $C_2$  molecule has in all 4 + 4 = 8 electrons and its molecular orbital configuration is  $(\sigma_{2s}^{b})^2, (\sigma_{2s}^{a})^2, (\pi_y^{b})^2 = (\pi_z^{b})^2$ , showing that  $n_b = 6$ ,  $n_a = 2$  and hence bond order = (6 - 2)/2 = 2, *i.e.* the two C-atoms in  $C_2$  molecule are joined together by two covalent bonds one of which is a  $\sigma$  bond and the other is a  $\pi$  bond. Since the molecular orbital configuration of  $C_2$  molecule does not have unpaired electron, this molecule is expected to be diamagnetic. Experimentally it has been found diamagnetic.

8. N<sub>2</sub> molecule  $(N \rightarrow 2s^2, 2p_x^{-1}, 2p_y^{-1}, 2p_z^{-1}, e = 10)$ . Each of the two N-atoms in N<sub>2</sub> molecule contributes 2 + 1 + 1 + 1 = 5 electrons and hence two N-atoms in N<sub>2</sub> molecule contribute  $5 \times 2 = 10$  electrons. The number of atomic orbitals used to form molecular orbitals is 4 + 4 = 8. Thus N<sub>2</sub> molecule has 8 molecular orbitals and 10 electrons to be accommodated in them. The molecular orbital configuration of N<sub>2</sub> molecule is :

$$(\sigma_{2s}^{\ b})^2$$
,  $(\sigma_{2s}^{\ a})^2$ ,  $(\pi_v^{\ b})^2 = (\pi_z^{\ b})^2$ ,  $(\sigma_r^{\ b})^2$ 

and its bond order is equal to  $\frac{1}{2}$  (8–2) = 3 which indicates that the molecule has one  $\sigma$  and two  $\pi$ -bonds. Bond order of three is in accordance with the very high bond energy (= 945.6 KJ. mole<sup>-1</sup>).

9.  $O_2$  molecule  $(O \rightarrow 2s^2, 2p_x^2, 2p_y^1, 2p_z^1, e = 12)$ . Each of two O-atoms in  $O_2$  molecule contributes 2 + 2 + 1 + 1 = 6 electrons and hence two O-atoms in  $O_2$  molecule contribute  $6 \times 2 = 12$  electrons. The number of molecular orbitals is 4 + 4 = 8. Thus  $O_2$  molecule has 8 molecular orbitals and 12 electrons to be accommodated in them. The molecular orbital configuration of  $O_2$  is :

$$(\sigma_{2s}^{\ b})^2, \ (\sigma_{2s}^{\ a})^2, \ (\pi_v^{\ b})^2 = (\pi_z^{\ b})^2, \ (\sigma_x^{\ b})^2, \ (\pi_y^{\ a})^1 = (\pi_z^{\ a})^1$$

Its bond order is equal to  $\frac{1}{2}(8-4) = 2$ . Thus O<sub>2</sub> molecule consists of a double bond which is composed of one  $\sigma$ - and one  $\pi$ -bond. It has bond dissociation energy = 493.7 KJ. mole<sup>-1</sup> and bond length = 1.21 Å. Its molecular orbital configuration as given above shows that it is paramagnetic due to the presence of two unpaired electrons which are in  $\pi_v^a$  and  $\pi_z^a$  molecular orbitals.

10. Oxygen molecule ion,  $O_2^-$  ( $O \rightarrow 2s^2p^4$ ,  $O^- \rightarrow 2s^2p^5$ , e = 13). Quite obviously this ion has 6 + 7 = 13 electrons in its valence-shell and hence its molecular orbital configuration is :

$$(\sigma_{2s}{}^b)^2$$
,  $(\sigma_{2s}{}^a)^2$ ,  $(\pi_y{}^b)^2 = (\pi_z{}^b)^2$ ,  $(\sigma_x{}^b)^2$ ,  $(\pi_y{}^a)^2 = (\pi_z{}^a)^1$ 

Thus its bond order is equal to  $\frac{1}{2}(8-5) = 1\frac{1}{2}$ . This value shows that one bond is a two-electron  $\sigma$ -bond and the other bond is one-electron  $\pi$ -bond.

11.  $F_2$  molecule  $(F \rightarrow 2s^2, 2p_x^2, 2p_y^2, 2p_z^1, e = 14)$ . Each of the two F-atoms in  $F_2$  molecule contributes 2 + 2 + 2 + 1 = 7 electrons and hence two F atoms in  $F_2$  molecule contribute  $2 \times 7 = 14$  electrons. The number of atomic orbitals used to form molecular orbitals is 4 + 4 = 8. Thus  $F_2$  molecule has 8 molecular orbitals and 14 electrons are to be accommodated in them. The molecular orbital configuration of  $F_2$  molecule is :

$$(\sigma_{2s}{}^{b})^{2}, \ (\sigma_{2s}{}^{a})^{2}, \ (\pi_{v}{}^{b})^{2} = (\pi_{z}{}^{b})^{2}, \ (\sigma_{x}{}^{b})^{2}, \ (\pi_{v}{}^{a})^{2} = (\pi_{z}{}^{a})^{2}.$$

This configuration shows that  $n_b = 8$ ,  $n_a = 6$  and hence bond order = (8 - 6)/2 = 1. Thus in F<sub>2</sub> molecule both F<sub>2</sub> atoms are linked to each other by a single bond. Since there are no unpaired electrons, F<sub>2</sub> molecule is *diamagnetic*.

12. Ne<sub>2</sub> molecule (Ne $\rightarrow$ 2s<sup>2</sup>, 2p<sub>x</sub><sup>2</sup>, 2p<sub>y</sub><sup>2</sup>, 2p<sub>z</sub><sup>2</sup>, e = 16). The molecular orbital configuration of Ne<sub>2</sub> molecule is :

 $(\sigma_{2s}{}^b)^2$ ,  $(\sigma_{2s}{}^a)^2$ ,  $(\pi_v{}^b)^2 = (\pi_z{}^b)^2$ ,  $(\sigma_x{}^b)^2$ ,  $(\pi_v{}^a)^2 = (\pi_z{}^a)^2$ ,  $(\sigma_x{}^a)^2$ .

This configuration shows that  $n_b = 8$ ,  $n_a = 8$  and hence bond order = (8 - 8)/2 = 0 which means that Ne<sub>2</sub> molecule does not exist.

# Molecular Orbital Configuration of Some Hetero-nuclear Diatomic Species

Hetero-nuclear diatomic species have two different atoms linked together. Thus these are AB type species. Here we shall consider those AB type species in which B has higher electronegativity than A and both the atoms A and B have 2sand 2p atomic orbitals, *i.e.* A and B are *p* block elements of second period of the periodic table.

The MO treatment of such types of hetero-nuclear diatomic molecules and molecule ions by LCAO approximation method is not fundamentally different from that of homo-nuclear diatomic molecules of  $A_2$  type, except that MOs are not

symmetric with respect to a plane perpendicular to and bisecting the internuclear axis.

Let us consider the following hetero-nuclear diatomic species.

**1. CO molecule**  $(C \rightarrow 2s^2p^2, O \rightarrow 2s^2p^4, e = 10)$ . Evidently CO molecule has 10 valence electrons : four from carbon atom  $(2s^2p^2)$  and six from oxygen atom  $(2s^2p^4)$ . Thus its molecular orbital configuration is :

$$(\sigma_{2s}^{\ b})^2, \ (\sigma_{2s}^{\ a})^2, \ (\pi_v^{\ b})^2 = (\pi_z^{\ b})^2, \ (\sigma_r^{\ b})^2$$

Thus its bond order is equal to  $\frac{1}{2}(8-2) = 3$ , showing that carbon and oxygen atoms in CO molecule are linked together by one  $\sigma$ -and two  $\pi$ -bonds. As is evident from the molecular orbital configuration, the molecule has no unpaired electron and hence it is diamagnetic.

**2. NO molecule**  $(N \rightarrow 2s^2p^3, O \rightarrow 2s^2p^4, e = 11)$ . This molecule has 11 electrons in its valence-shell : five from nitrogen atom  $(2s^2p^3)$  and six from oxygen atom  $(2s^2p^4)$ . Thus it has the following molecular orbital configuration :

$$(\sigma_{2s}{}^{b})^{2}, \ (\sigma_{2s}{}^{a})^{2}, \ (\pi_{v}{}^{b})^{2} = (\pi_{z}{}^{b})^{2}, \ (\sigma_{x}{}^{b})^{2}, \ (\pi_{v}{}^{a})^{1} = (\pi_{z}{}^{a})^{0}$$

The configuration given above shows that  $n_b = 8$ ,  $n_a = 3$  and hence bond order =  $(8 - 3)/2 = 2\frac{1}{2}$  Bond order equal to  $2\frac{1}{2}$  means that N and O atoms in NO molecule are linked together by one  $\sigma$  bond (due to the presence of electron pair in  $\sigma_r^{\ b}$  molecular orbital) and two  $\pi$  bonds (due to the presence of two electron pairs in  $\pi_y^{\ b}$  and  $\pi_z^{\ b}$  molecular orbitals) less the effect of one unpaired electron present in  $\pi_v^a$  molecular orbital. In other words we can say that NO molecule has two 2-electron bonds and one 3-electron bond and can, therefore, be represented as :  $N \stackrel{\leftrightarrow}{=} O_X^{\times}$ . The presence of one unpaired electron in  $\pi_y^a$  molecular orbital makes NO molecule less stable than N2 molecule. This is confirmed by the fact that bond dissociation energy of NO molecule (= 667.8 KJ/mole) is less than that of N<sub>2</sub> molecule (= 945.6 KJ/mole). The presence of one unpaired electron also accounts for the paramagnetic nature of NO molecule. Molecular orbital configuration of NO molecule as given above also explains that it should be easy for this molecule to form nitrosonium ion (NO<sup>+</sup>) by losing one electron residing in  $\pi_v^a$  molecular orbital and NO<sup>+</sup> ion so produced should have shorter and hence stronger nitrogen-oxygen bond. The experimental values of nitrogen-oxygen bond length and bond energy for these species as given below confirm this fact.

$N = O_{\times}^{\times}$	$\begin{bmatrix} : N \equiv O_{\times}^{\times} \end{bmatrix}^{+}$	
1.14 A°	1.06 A°	
667.8 KJ/mole	1019.9 KJ/mole	

3. Nitrosyl ion, NO<sup>+</sup> (N $\rightarrow 2s^2p^3$ , O<sup>+</sup> $\rightarrow 2s^2p^3$ , e = 10). As is evident, this ion has 5 + 5 = 10 electrons and its molecular orbital configuration is :  $(\sigma_{2s}{}^b)^2$ ,  $(\sigma_{2s}{}^a)^2$ ,  $(\pi_y{}^b)^2 = (\pi_z{}^b)^2$ ,  $(\sigma_x{}^b)^2$ , showing that its bond order = (8 - 2)/2 = 3, *i.e.* this ion has one  $\sigma$  and two  $\pi$  bonds,  $: N \equiv O^+$ : or  $[:N \equiv O^+]^+$ . Since the ion has no unpaired electron, it has diamagnetic character.

## Valency Bond Theory vs Molecular Orbital Theory

## (A) Similarities

(i) Both the theories are the interpretation of covalent bond.

(ii) According to both the theories the AOs of the two atoms must overlap to form a covalent bond. The AOs overlapping each other must have the same symmetry and must be of the same energy.

(*iii*) According to both, the electronic charge resides in the region between the atomic nuclei.

(iv) Both the theories postulate that a covalent bond possesses directional properties.

### **(B) Differences**

MOT	VBT
<ul> <li>(i) MOs are formed by LCAO approximation method. The AOs involved in the formation of these MOs are from valence shell of two atoms.</li> </ul>	<ul> <li>(i) Two AOs give an interatomic orbital obtained by the combi- nation of the space functions of two unpaired electrons; one being in each of the two AOs.</li> </ul>
<ul><li>(ii) AOs of the resulting molecule lose their individual identity.</li></ul>	<ul> <li>(ii) The resulting molecule consists of atoms which, although, inter- acting, retain a large measure of their individual character.</li> </ul>
( <i>iii</i> ) MOT starts with the nuclei of the constituent atoms.	(iii) VBT starts with the individual atoms and considers the inter- action between them.
( <i>iv</i> ) MOT offers a satisfactory explanation of the paramagnetic character of $O_2$ molecule.	(iv) VBT fails to account for the paramagnetic character of $O_2$ molecule.
(v) Resonance plays no role in MOT.	(v) Resonance plays an important role in VBT.

# **Questions with Answers**

Q.1 We are given some molecules / ions that have been grouped into four pairs :

(i)  $BrO_3^{-}$ ,  $XeO_3$  (ii)  $SF_4$ ,  $XeF_4$  (iii)  $SO_3^{2-}$ ,  $NO_3^{-}$  (iv)  $BF_3$ ,  $NF_3$ . Out of these pairs which pair is isostructural ?

Ans : The structure of the given pairs are given below :

(*ii*)

SF.  $\sigma$ -bps + lps = 4 + 1 = 5  $\sigma$ -bps + lps = 4 + 2 = 6

 $\mathbf{F}_{\mathbf{F}} > \mathbf{\ddot{s}} < \mathbf{F}_{\mathbf{F}}$   $\mathbf{F}_{\mathbf{F}} > \mathbf{\ddot{x}} < \mathbf{F}_{\mathbf{F}}$ 

XeF (See-saw geometry) (Square planar)

 $\sigma$ -bps + lps = 3 + 1 = 4 (Trigonal pyramidal) (Trigonal planar)

BF.  $\sigma$ -bps + lps = 3 + 0 = 3

(Trigonal planar)

(iv) F-B-F

 $\bar{O} - \ddot{S} - \bar{O}$  $\parallel O$  $SO_3^{2-}$ 

$$\begin{array}{c} \bar{O} - N \rightarrow O \\ \parallel \\ O \\ NO_3^{-} \end{array}$$

 $\sigma$ -bps + lps = 3 + 0 = 3

F-N-F | F NF<sub>3</sub>

 $\sigma$ -bps + lps = 3 + 1 = 4 (Trigonal pyramidal)

Since BrO<sub>3</sub><sup>-</sup> - XeO<sub>3</sub> pair has the same geometry (trigonal pyramidal), this pair is isostructural.

Q.2 How many sigma ( $\sigma$ ) and pi ( $\pi$ ) bonds are there in allyl isocyanide? Ans : The radical obtained by removing H-atom from propence (also called

propylence),  $CH_2 = CH - CH_3$  is called allyl radical. This radical has positive charge.

 $CH_2 = CH - CH_3 \xrightarrow{-H} CH_2 = CH - \overset{+}{CH_2}$ Propene or propylene Allyl radical

Obviously the structure of allyl isocyanide molecule can be written as :

н	н	н	Isocyanide ion
σ	σ	σ	·
$C = \pi$	$= C - \sigma$	- C -	N = C:
ο H		H (	π

Obviously ally isocyanide has  $9\sigma$  and  $3\pi$  bonds.

Q.3 (a) Calculate bond order (B.O.) in NO2<sup>+</sup>, NO2<sup>-</sup>, NO3<sup>-</sup>, CO3<sup>2-</sup> and  $N_3^-$  ions.

(b) Compare the nitrogen-oxygen bond lengths in NO2<sup>+</sup>, NO2<sup>-</sup> and NO3<sup>-</sup> ions.

**Ans** : (a) We know that :

B.O. of a given specices showing resonance

Total number of bonds between two specific

atoms in all the resonating structures

Total number of resonating structures

(i)  $NO_2^+$  ion. This ion shows resonance. It is a resonance hybrid of the following two resonating structures.

 $: \ddot{O}_a = \overset{+}{N} \rightarrow \ddot{O}: \leftrightarrow : \ddot{O}_a = \overset{+}{N} = \ddot{O}:$ (I)

Total number of bonds between N and O<sub>a</sub> atoms :. Bond order of  $NO_2^+$  ion =  $\frac{\text{in the two resonating structures shown above}}{T_1 + 1}$ 

$$=\frac{2+2}{2}=\frac{4}{2}=2$$
 (Ans.)

(ii)  $NO_2^-$  ion. This ion is a resonance hybrid of the following two resonating structures.

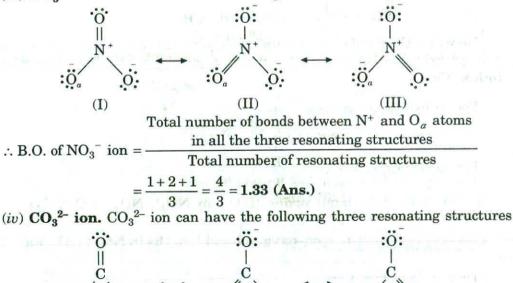


Total number of bonds between N and O<sub>a</sub> atoms in the two resonating structures

 $\therefore$  B.O. of NO<sub>2</sub><sup>-</sup> ion = Total number of resonating structures

$$=\frac{1+2}{2}=\frac{3}{2}=1.5$$
 (Ans.)

(iii) NO<sub>3</sub><sup>-</sup> ion. This ion has the following three resonating structures.



 $(\mathbf{I})$ 

(III)

 $\therefore B.O. of CO_3^{2^-} ion = \frac{\text{Total number of bonds between C and } O_a \text{ atoms}}{\text{Total number of resonating structures}}$   $\frac{1+2+1}{4} = \frac{4}{4}$ 

 $=\frac{1+2+1}{3}=\frac{4}{3}=1.33$  (Ans.)

(v)  $N_3^-$  ion. (Azide ion). We know that this ion is a resonance hybrid of the following three structures

$$: \ddot{\ddot{N}}_{a} = \overset{+}{N} = \ddot{\ddot{N}}: \longleftrightarrow : \overset{-2}{\ddot{N}}_{a} - \overset{+}{N} \equiv \ddot{\ddot{N}} \iff : N_{a} \equiv \overset{+}{N} - \overset{-2}{\ddot{N}}:$$
(II)
(III)

Total number of bonds between  $N_{\sigma}$  atom and the  $\therefore$  B.O. of  $N_3^-$  ion =  $\frac{\text{central } \dot{N}\text{-atom in all the three resonating structures}}{\text{Total number of resonating structures}}$ 

$$=\frac{2+1+3}{3}=\frac{6}{3}=2$$
 (Ans.)

(b) Since B.O. of NO<sub>2</sub><sup>+</sup>, NO<sub>2</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup> ions is in the order : NO<sub>2</sub><sup>+</sup> (B.O. = 2.00) > NO<sub>2</sub><sup>-</sup> (B.O. = 1.50) > NO<sub>3</sub><sup>-</sup> (B.O. = 1.33), nitrogen-oxygen bond lengths are in the reverse order, *i.e.*nitrogen-oxygen bond lengths are in the order : NO<sub>2</sub><sup>+</sup> (= 1.55 Å<sup>o</sup>) < NO<sub>2</sub><sup>-</sup> (= 1.22 Å<sup>o</sup>) < NO<sub>3</sub><sup>-</sup> (= 2.18 Å<sup>o</sup>)

Q.4 (i) Calculate (a) Angle between two sp hybrid obitals (sp hybridisation) and three  $sp^2$  hybrid orbitals ( $sp^2$  hybridsation) (b) % s-character in sp,  $sp^2$  and  $sp^3$  hybrid orbitals (*ii*) Arrange the given hybrid orbitals in the decreasing order of percentage of s-character in them.

**Ans**: (i) (a) Angle ( $\infty$ ) between two hybrid orbitals is given by :

$$\cos \propto = -\frac{1}{m}$$

Here *m* is the number of *p*-orbitals that take part in hybridisation. For sp,  $sp^2$  and  $sp^3$  hybridisation m = 1, 2 and 3 respectively. *m* is called **hybridisation** index. Thus :

For sp hybridisation  $\cos \infty = -\frac{1}{m} = -\frac{1}{1}$  $\therefore \infty = 180^{\circ}$  (Ans)

For  $sp^2$  hybridisation  $\cos \infty = -\frac{1}{m} = -\frac{1}{2}$ 

$$\infty = 120^{\circ}$$
 (Ans)

(b) % s-character is given by :

% s-character = 
$$\frac{1}{1+m} \times 100$$

Thus :

% s-character in sp hybrid orbitals

$$= \frac{1}{1+1} \times 100 = 50\% \text{ (Ans)}$$

% s-character in  $sp^2$  hybrid orbitals

$$=\frac{1}{1+2}$$
 × 100 = 33.3% (Ans)

% s-character in  $sp^3$  hybrid orbitals

$$=\frac{1}{1+3}$$
 × 100 = 25% (Ans)

(ii) Obviously the decreasing order of the percentage of s-character is :

$$sp (= 50\%) > sp^2 (= 33.3\%) > sp^3 (= 25\%)$$

Q.5 Bond order of CO<sup>+</sup> ion is higher than that of CO molecule. Explain OR

Carbon-oxygen bond length in CO<sup>+</sup> ion is lower than that in CO molecule. Explain.

Ans: We know that the MOEC of CO molecule (e = 4 + 6 = 10) is:

$$(\sigma_{2s}^{\ b})^2 (\sigma_{2s}^{\ a})^2 (\pi_y^{\ b})^2 = (\pi_z^{\ b})^2 (\sigma_x^{\ b})^2$$
  
 $\therefore$  B.O. of CO =  $\frac{n_b - n_a}{2} = \frac{8 - 2}{2} = 3$ 

In case of CO<sup>+</sup> ion it has been suggested that 2s orbital of C-atom has higher energy than 2s orbital of O-atom. When these 2s orbitals mix together to form  $\sigma_{2s}{}^{b}$  and  $\sigma_{2s}{}^{a}$  MOs,  $\sigma_{2s}{}^{a}$  MO has so high energy that it occupies a position in the energy level diagram above  $\pi_{y}{}^{b}$ ,  $\pi_{z}{}^{b}$  and  $\sigma_{x}{}^{b}$  MOs. Thus MOEC of CO<sup>+</sup> ion (e = 4 + 6 - 1 = 9) is :

$$(\sigma_{2s}{}^{b})^{2} (\pi_{v}{}^{b})^{2} = (\pi_{z}{}^{b})^{2} (\sigma_{x}{}^{b})^{2} (\sigma_{2s}{}^{a})^{1}$$

: B.O. of CO<sup>+</sup> = 
$$\frac{n_b - n_a}{2} = \frac{8 - 1}{2} = 3.5$$

Obviously B.O. of CO<sup>+</sup> ion (= 3.5) is higher than that of CO molecule (= 3). It is because of higher B.O. of CO<sup>+</sup> ion that the carbon-oxygen bond length in CO<sup>+</sup> ion (= 1.115 A°) is lower than carbon-oxygen bond length in CO molecule (= 1.128 A°).

Q.6 Explain the following, giving appropriate reasons.

(i)  $H_2^+$  and  $H_2^-$  ions have the same bond order (= 0.5), yet  $H_2^-$  ion is slightly less stable than  $H_2^+$  ion.

(*ii*)  $N_2$  has greater bond dissociation energy than  $N_2^+$  whereas  $O_2^+$  has greater bond dissociation energy than  $O_2$ .

(*iii*) Bond in  $H_2^+$  is larger than that in  $H_2$ .

(*iv*) Superoxide ion  $(O_2^{-})$  is paramagnetic but peroxide ion  $(O_2^{2-})$  is not.

(v) Sigma bond in  $H_2$  molecule (H - H) is stronger than that in  $Li_2$  molecule (Li - Li).

(vi) Out of H and H<sub>2</sub>, the latter has higher IE while out of O and O<sub>2</sub>, the former has higher IE.

**Ans** : (i) MOECs of  $H_2^+$  and  $H_2^-$  ions are as :

 $H_2^+$  ion  $(e = 1 + 1 - 1 = 1) = (\sigma_{1s}^{b})^1 (\sigma_{1s}^{a})^0 (n = 1)$ 

 $H_2^-$  ion  $(e = 1 + 1 + 1 = 3) = (\sigma_{1s}^{\ b})^2 \ (\sigma_{1s}^{\ a})^1 \ (n = 1)$ 

These configurations show that  $H_2^-$  ion contains one unpaired electron in antibonding MO ( $\sigma_{1s}^{a}$ ) which produces destablising effect and hence decreases the stability of  $H_2^-$  ion. On the other hand  $H_2^+$  ion does not contain any electron in antibonding MO.

(ii) MOECs and BOs of the given species are given below :

Species	MOECs	B.O.
$N_2 (e = 10)$	$(\sigma_{2s}^{\ b})^2 \ (\sigma_{2s}^{\ a})^2 \ (\pi_y^{\ b})^2 = (\pi_z^{\ b})^2 \ (\sigma_x^{\ b})^2$	$\frac{8-2}{2} = 3$
$N_2^+ (e = 9)$	$(\sigma_{2s}^{\ b})^2 \ (\sigma_{2s}^{\ a})^2 \ (\pi_y^{\ b})^2 = (\pi_z^{\ b})^2 \ (\sigma_x^{\ b})^1$	$\frac{7-2}{2} = 2.5$
$O_2 (e = 12)$	$(\sigma_{2s}{}^{b})^{2} (\sigma_{2s}{}^{a})^{2} (\pi_{y}{}^{b})^{2} = (\pi_{z}{}^{b})^{2} (\sigma_{x}{}^{b})^{2} (\pi_{y}{}^{a})^{1} = (\pi_{z}{}^{a})^{1}$	$\frac{8-4}{2}=2$
$O_2^+ (e = 11)$	$(\sigma_{2s}{}^{b})^{2} (\sigma_{2s}{}^{a})^{2} (\pi_{y}{}^{b})^{2} = (\pi_{z}{}^{b})^{2} (\sigma_{x}{}^{b})^{2} (\pi_{y}{}^{a})^{1} = (\pi_{z}{}^{a})^{0}$	$\frac{8-3}{2} = 2.5$

Since  $(B.O.)_{N_2}$  (= 3.0) >  $(B.O.)_{N_2^+}$  (= 2.5), N<sub>2</sub> has greater bond dissociation energy. On the other bond, since  $(B.O.)_{O_2^+}$  (= 2.5) >  $(B.O.)_{O_2}$  (= 2.0), O<sub>2</sub><sup>+</sup> has greater bond dissociation energy.

(*iii*) MOECs and BOs of  $H_2^+$  and  $H_2$  are :

$$H_{2}^{+} (e = 2 - 1 = 1) = (\sigma_{1s}^{b})^{1}, (B.O.)_{H_{2}}^{+} = \frac{1}{2} = 0.5$$
$$H_{2} (e = 2) = (\sigma_{1s}^{b})^{2}, (B.O.)_{H_{2}}^{-} = \frac{2}{2} = 1.0$$

Now since  $(B.O.)_{H_2}^+$  (= 0.5) <  $(B.O.)_{H_2}^-$  (= 1.0), bond in  $H_2^+$  is larger than that in  $H_2$ .

(*iv*) MOECs of  $O_2^-$  and  $O_2^{2-}$  ion are given below :

$$\begin{split} \mathbf{O_2^-} &(e=6\times2+1=13) = (\sigma_{2s}{}^b)^2 \ (\sigma_{2s}{}^a)^2 \ (\pi_y{}^b)^2 = (\pi_z{}^b)^2 \ (\sigma_x{}^b)^2 \\ &(\pi_y{}^a)^2 = (\pi_z{}^a)^1 \ (n=1) \\ \mathbf{O_2^{2^-}} &(e=6\times2+2=14) = (\sigma_{2s}{}^b)^2 \ (\sigma_{2s}{}^a)^2 \ &(\pi_y{}^b)^2 \\ &= (\pi_z{}^b)^2 \ (\sigma_x{}^b)^2 \ (\pi_y{}^a)^2 = (\pi_z{}^a)^2 \ (n=0) \end{split}$$

Now since  $O_2^-$  ion has one unpaired electron (n = 1), this ion is paramagnetic. On the other hand since  $O_2^{2-}$  ion does not have any paired electron, this ion not paramagnetic. Rather,  $O_2^{2-}$  ion is diamagnetic.

(v) On the basis of MO theory, MO configuration of  $H_2$  and  $Li_2$  molecules can be written as :

$$H_2 (e = 2) = (\sigma_{1s}{}^b)^2, (B.O.)_{H_2} = \frac{2-0}{2} = 1$$
  
$$Li_2 (e = 2) = (\sigma_{2s}{}^b)^2, (B.O.)_{Li_2} = \frac{2-0}{2} = 1$$

Bond order equal to 1 indicates that the two atoms in both the molecules are bonded together by a single sigma bond. Thus these molecules can be represented as H–H and Li–Li respectively. It has been observed that in H<sub>2</sub> molecule H–H bond length = 0.74 Ű and bond dissociation energy = 458 KJ mol<sup>-1</sup>. Similary, in Li<sub>2</sub> molecule, Li – Li bond length = 2.67 Ű and bond dissociation energy = 105 KJ mol<sup>-1</sup>. These values show that H–H sigma bond in H<sub>2</sub> molecule is stronger than Li – Li bond in Li<sub>2</sub> molecule. This has been explained as follows.

**Explanation :** (a) Since 2s orbital of Li-atom is larger in size than 1s orbital of H-atom, 2s - 2s overlap in Li<sub>2</sub> molecule is less effective than 1s - 1s overlap in H<sub>2</sub> molecule. These overlaps give  $\sigma_{2s}{}^{b}$  and  $\sigma_{1s}{}^{b}$  molecular orbitals in Li<sub>2</sub> and H<sub>2</sub> molecules respectively.

(b) In Li<sub>2</sub> molecule, the outer two electrons present in  $\sigma_{2s}^{b}$  MO are shielded by the inner four electrons present in two 1s orbitals on two Li atoms. Therefore, the attraction between the nuclei and the two electrons in  $\sigma_{2s}^{b}$  MO is less.

(vi) The configurations of given species are given below :

H (e = 1) = 1s<sup>1</sup>, H<sub>2</sub> (e = 1 × 2 = 2) =  $(\sigma_{1s}^{\ \ b})^2$ 

O  $(e = 6) = 2s^2 2p^4$ , O<sub>2</sub>  $(e = 2 \times 6 = 12) = (\sigma_{2s}{}^b)^2 (\sigma_{2s}{}^a)^2 (\pi_y{}^b)^2 = (\pi_z{}^b)^2 (\sigma_x{}^b)^2 (\pi_y{}^b)^2 = (\pi_z{}^b)^2 (\sigma_x{}^b)^2 (\pi_y{}^b)^2$ 

In H-atom electron is to be removed from 1s AO while in H<sub>2</sub> molecule electron is to be removed from  $\sigma_{1s}{}^{b}$  MO. Now since  $\sigma_{1s}{}^{b}$  MO has lower energy (more stable) than 1s AO, H<sub>2</sub> molecule has higher IE than H-atom.

In O-atom electron has to be removed from 2p AO while in O<sub>2</sub> molecule electron has to be removed from  $\pi_y^a$  or  $\pi_z^a$  MO. Now since 2p AO of O-atom has lower energy (more stable) than  $\pi_y^a$  or  $\pi_z^a$  MO in O<sub>2</sub> molecule, O-atom has higher IE than O<sub>2</sub> molecule.

# University Questions

- 1. Mention any two exceptions of VSEPR theory. (Punjab B.Sc. 1986)
- Distinguish two aspects of the following : (i) Atomic and molecular orbital (ii) Bonding and anti bonding MO. (iii) Sigma and pi MO.

(Himachal Pradesh 2000)

- In which of the following species sulphur does not undergo sp<sup>3</sup> hybridisation ? SO<sub>4</sub><sup>2-</sup>, H<sub>2</sub>S, SF<sub>4</sub> and SF<sub>2</sub>. (Himachal Pradesh 2000)
- 4. Discuss the structures of  $ICl_2^-$ ,  $SO_4^{2-}$  and  $Cl_2O$ .

(Himachal Pradesh 2000)

 What is hybridisation? On the basis of hybridisation of orbitals deduce the shape of PCl<sub>5</sub>, SF<sub>6</sub> and NH<sub>3</sub> molecules. (Kanpur 2000)

- 6. Give an account of sp,  $sp^2$  and  $sp^3$  hybridisation. (Kumaon 2000)
- 7. Give the structure of the following with the help of orbital diagram : PCl<sub>5</sub>, ICl<sub>4</sub><sup>-</sup>, XeOF<sub>4</sub> and SOCl<sub>2</sub> (Lucknow 2000)
- 8. (a) What do you understand by hybridisation? Describe its important features.
  - (b) Deduce the shapes of following molecules and predict the bond angle in each case. (i) BF<sub>3</sub> (ii) NH<sub>3</sub> (iii) H<sub>2</sub>O. (Avadh 2000)
- **9.** Draw and explain the structures of  $BF_3$ ,  $PCl_5$ ,  $SF_6$  and  $XeF_6$  on the basis of VSEPR theory. (Bharathiar 2000)
- 10. (i) Explain why hydrogen forms diatomic molecule while helium remains monoatomic.
  - (ii) Give the salient features of VSEPR theory and discuss the shape of  $ICl_3$ ,  $XeF_4$ ,  $PCl_5$  and  $TeCl_4$  molecules with the help of this theory.
  - (*iii*) Use MO theory to predict the bond order and the number of unpaired electrons in  $O_2^{2-}$ ,  $O_2$ ,  $O_2^+$ , NO and CO. (Lucknow 2001)
- 11. (a) What is the basic difference in valence bond theory and molecular orbital theory? Draw MO. diagram and discuss stability, electronic configuration and characteristics of the following :

Be<sub>2</sub>, He<sub>2</sub><sup>+</sup>, N<sub>2</sub> and O<sub>2</sub>.

(b) Explain the term hybridisation. Discuss the structure, shape and bond angles of the following molecules:  $BF_3$ ,  $SiF_4$ ,  $NH_3$ ,  $H_2O$  and  $PCl_5$ .

(Lucknow 2001)

- 12. (a) What is hybridisation ? On the basis of hybridisation of orbitals, leduce the shape of the following molecuels / ions :  $H_3O^+$ ,  $BF_3$ ,  $CIF_3$  and  $SF_4$ 
  - (b) On the basis MOT calculate B.O. of :  $He_2^+$ ,  $O_2^-$ ,  $N_2^+$ ,  $F_2^-$ ,  $B_2$

(Purvanchal 2007)

- 13. Which of the following compounds shows  $sp^2$  hybridisation? BeCl<sub>2</sub>, BF<sub>3</sub>, PCl<sub>5</sub> and FF<sub>7</sub>. (Agra 2008)
- 14. (a) In  $sp^2$  hybridisation, the value of bond angle is : 120°, 109°28', 180° or 108°.
  - (b) The state of hybridisation of S-atom of  $SO_2$  molecule is :  $sp^2$ , sp,  $dsp^2$  or  $sp^3$ . (H.N. Bhauguna 2008)
- 15. (a) There is  $sp^3$  hybridisation in methane, ammonia and water but their bond angles are different Explain.
- (b) O<sub>2</sub> is paramagnetic but N<sub>2</sub> is diamagnetic. Explain. (Meerut 2008)
   16. Discuss MOT of chemical bonding. Describe the MOC of O<sub>2</sub>, N<sub>2</sub> and CD molecules. (Meerut 2009)

CHAPTER

# Structure of Solids

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# Crystalline and Amorphous Solids : Classification of Solids on the Basis of Regular or Haphazard Arrangement of the Building Constituents.

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1. Crystalline solids. In crystalline solids the building constituents (atoms, ions or molecules) arrange themselves in a *three dimensional recurring regular* geometric pattern which extends to very large distance compared to the interparticle distances. Thus the crystalline solids have *long-range order*.

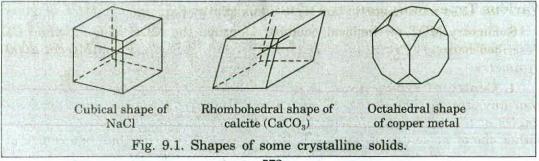
Crystalline solids exist as crystals and hence these are also called simply crystals. These crystals may be big or small. Some crystals are so tiny that their crystalline shape can be seen with a microscope only. A crystalline solid has a sharp melting point.

2. Amorphous solids. The word amorphous is a Greek word which means *shapeless*. Thus in these solids the arrangement of different building constituents is *not regular* but *haphazard i.e.* the constituents are arranged at random in the same disorderly way as in liquids. It is for this reason that amorphous substances like glass, pitch and resins are regarded as *super-cooled liquids* or *as intermediate between solids and liquids*. An amorphous substance does not have a sharp melting point.

### **Differences between Crystalline and Amorphous Solids**

These two classes of solids differ from one another in the following properties. **1. Geometrical shape.** The crystals of every crystalline solid have a *define* geometrical shape due to definite and orderly arrangement of particles in threedimensional shape, *e.g.* crystals of NaCl have a *cubical shape*, those of *calcite* (CaCO<sub>3</sub>) have *rhombohedral shape* while those of *copper* metal have an *octahedral* shape. (Fig. 9.1).

For a given crystal the angles at which the surfaces or faces intersect are always the same.



Most of the crystalline solids are *poly crystals. i.e.* they contain aggegate of many inter-locking small crystals. Such solids have irregular shape but their internal structure is regular. *Mono crystals (i.e. single crystals)* are sometimes found in nature. They can also be prepared by artificial means. Sugar is an example of a crystal composed of many single crystals.

An amorphous solid does not have any orderly pattern of arrangement of particles and, therefore, does not have any definite geometrical shape.

2. Melting point. There are many crystalline solids which do not change directly to the liquid state and also there are many crystalline solids which decompose before going into the liquid state. The crystalline solids which directly change into liquid state do so at a definite temperature *i.e.* the melting point of such crystalline solids is *definite*.

Amorphous substances like glass do not have definite melting point.

**3.** Cleavage planes. When a crystal of a crystalline solid is hammered, it readily breaks up into smaller crystals along particular planes which are called *cleavage planes*. These planes are inclined to one another at a particular angle for a given crystalline solid. Thus the magnitude of this angle varies from substance to substance.

Amorphous substances do not have such well-defined cleavage planes.

4. Anisotropic and isotropic properties. Magnitude of some of the physical properties of crystalline solids like refractive index, coefficient of thermal expansion, electrical and thermal conductivities etc. is different in different directions within the crystal, *e.g.* the coefficient of thermal expansion of a crystal of AgI is positive in one direction and negative in the other direction. Such properties are called *anisotropic properties* and the phenomenon is referred to as *anisotropy*. These properties are due to the fact that the orderly arrangement of particles in crystalline solids is different in different directions.

The above said properties of isomorphous substances are the same in all directions as those of liquids and gases, *i.e. amorphous substances have isotropic properties.* This is because of the fact that in isomorphous solids, as in liquids and gases, the arrangement of particles is random and, therefore their isotropic properties are the same in all the directions.

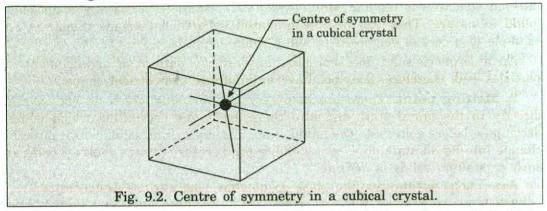
**5.** Symmetry. Crystalline solids have crystal symmetry, *i.e.* when a crystalline solid is rotated about an axis, its appearance does not change (*i.e.* remains the same).

Amorphous substances do not have symmetry.

### Various Types of Symmetry Found in Crystals

Symmetry is a very important property of crystals. Only three of these are described here. (1) Centre of symmetry (2) Axis of symmetry, and (3) Plane of symmetry.

1. Centre of symmetry. It is such an imaginary point within the crystal that any straight line drawn through it will intersect the faces, edges or solid angles of the crystal at equal distances on opposite sides. A crystal may have either one or no centre of symmetry. It can never have more than one centre of symmetry. A cubical crystal like NaCl crystal has one centre of symmetry as shown in Fig. 9.2.

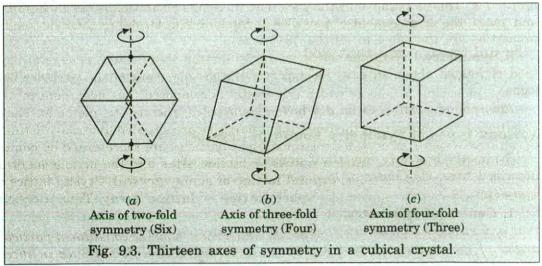


**2.** Axis of symmetry. It is an imaginary straight line about which, if the crystal is rotated, it will present the same appearance more than once during its complete rotation.

In all there are thirteen axes of symmetry possessed by a cubical crystal like NaCl as shown below :

(a) Six axes of two-fold symmetry. Each of these six axes is called diad axis. When the crystal is rotated about any of these axes, it presents the same appearance two times in a complete rotation. One of such axes is shown in Fig. 9.3(a). Each of these three axes intersects at the middle points of the two opposite edges of the cube.

(b) Four axes of three-fold symmetry. Each of these axes is called *triad axis*. When the crystal is rotated about any of these axes, it presents the same appearance *three times* in a complete rotation. One of such axes is shown in Fig. 9.3(b). Each of these four axes intersects at the two opposite solid angles (*i.e.* corners) of the cube.



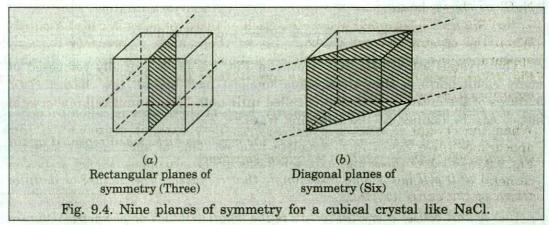
(c) Three axes of four-fold symmetry. Each of these three axes is called *tetrad* axis. When the crystal is rotated about any of these axes, it presents the same appearance four times in a complete rotation. One of such axes is shown in Fig. 9.3(c). Each of these three axes intersects at the middle points of the two opposite faces of a cube. All the three axes are at right angles to one another.

**3.** Plane of symmetry. It is an imaginary plane which divides a crystal into two such parts that one is the exact mirror image of the other. In other words, a plane of symmetry divides the crystal into two identical and similarly placed halves.

In all, there are nine planes of symmetry possessed by a cubical crystal like NaCl as shown below :

(a) Three rectangular planes of symmetry. One such rectangular plane of symmetry is shown in Fig. 9.4(a). There are in all three such rectangular planes of symmetry which are at right angles to each other.

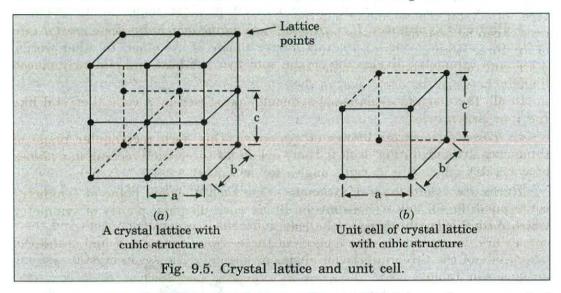
(b) Six diagonal planes of symmetry. One such diagonal plane of symmetry is shown in Fig. 9.4 (b). There are in all six such diagonal planes of symmetry which pass diagonally through the cube.



#### **Crystal Lattice and Unit Cell**

The internal structure of crystals (*i.e.* the arrangement of the particles *viz.* atoms, molecules or ions of which the crystal is composed) has been determined by *X-ray diffraction, electron diffraction, neutron diffraction* etc. methods. These methods have shown that the constituent particles are situated at strictly definite positions in space. In crystals, the constituent particles are represented by points. These points are called **lattice points** or **lattice sites** and the arrangement of points in the crystal is called **crystal lattice** or simply **crystal**. Crystal lattice is also called by other names like **space lattice** or **lattice array**. Thus a crystal lattice can be defined as follows :

A crystal lattice is an array of points which show how the constituent particles (atoms, ions or molecules) of a crystal are arranged at different sites in threedimensional space. In other words a crystal lattice is an infinitely extended regular arrangement of different constituent particles of a crystal. Each point in a crystal lattice has the same environment as any other similar point. A crystal lattice with cubic structure with three-dimensional net work is shown in Fig. 9.5 (a).



The crystal lattice like that shown in Fig. 9.5 (a) is actually composed of many small parts of the lattice. This smallest part has all the characteristic features of the entire crystal and is called **unit cell**. Thus a unit cell of a crystal lattice can be defined in the following ways :

(i) A unit cell is the smallest unit of the crystal which, when repeated again and again, gives the crystal of the given substance.

(ii) A unit cell is the smallest sample that represents the picture or definite pattern of the entire crystal.

(iii) A unit cell of a crystal lattice is the smallest block or geometrical figure from which the entire crystal can be built up by its translational repetition in three dimensions.

Thus the entire crystal consists of a large number of unit cells adjacent to one another in all three dimensions. The unit cell of the crystal lattice shown in Fig. 9.5 (a) is shown in the same figure at (b).

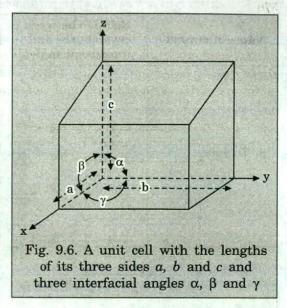
A unit cell of a crystal possesses all the structural properties of the given crystal. A large number of unit cells of the crystal combine together to arrange themselves in a regular order and thus form the crystal lattice.

It may be noted that the properties of crystalline solids depend not only on their composition and external conditions, but also on their internal structure. For example, although diamond and graphite are composed of the same substance *viz.*, carbon, they have different properties. The difference in their properties is due to the difference in their internal structure.

#### Seven Crystal Systems

Depending on the nature of the constituents (which may be atoms, molecules or ions) of which a given crystal is composed, we have different types of crystal. The shape of a given crystal can be described by the lengths of the three sides or edges (a, b and c) of its unit cell and the three angles  $(\alpha, \beta \text{ and } \gamma)$  between the three axes of the unit cell are called *primitives* or *crystal axes* and the angles between the three axes are called *interfacial angles* (See Fig. 9.6).

There are seven crystal systems corresponding to the seven distinct

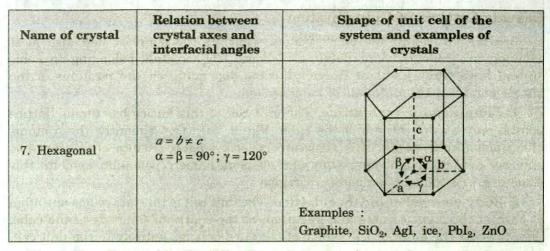


types of unit cells (sub-units). All these unit cells are parallelopipeds and their shapes are determined by the lengths of three crystal axes, a, b and c and the magnitude of the three interfacial angles  $\alpha$ ,  $\beta$  and  $\gamma$ . The seven crystal systems are given in Table 9.1.

Name of crystal	Relation between crystal axes and interfacial angles	Shape of unit cell of the system and examples of crystals	
1. Cubie	$\alpha = \delta = c$ $\alpha = \beta = \gamma = 90^{\circ}$	Examples : NaCl, KCl, CaF <sub>2</sub> , NaClO <sub>2</sub> alums,	
unit allegation of Allegation description		diamond	
2. Monoclinic	$a \neq b \neq c$ $\alpha = \beta = 90^{\circ}; \gamma \neq 90^{\circ}$	$\beta \overset{\alpha}{\longrightarrow} \overset{b}{\longrightarrow} \overset{b}{\longrightarrow}$	
a statisti ana ana ana ana a statisti ang ang ang ang		Examples : $Na_2SO_4.10H_2O$ , $NaHCO_3$ , $FeSO_4$ , $7H_2O$ , monoclinic sulphur (SM)	

Table 9.1. Seven systems of crystals

Name of crystal	Relation between crystal axes and interfacial angles	Shape of unit cell of the system and examples of crystals
3. Triclinic	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma \neq 90^{\circ}$	Examples : CuSO <sub>4</sub> .5H <sub>2</sub> O, K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> , H <sub>3</sub> BO <sub>3</sub>
4. Tetragonal	$a = \delta \neq c$ $\alpha = \beta \neq \gamma = 90^{\circ}$	Examples : NiSO <sub>4</sub> , white tin, SnCl <sub>2</sub> , TiO <sub>2</sub> etc.
5. Orthorhombic or Rhombic	$a = b \neq c$ $\alpha = \beta = \gamma = 90^{\circ}$	Examples : KNO <sub>3</sub> , BaSO <sub>4</sub> , MgSO <sub>4</sub> .7H <sub>2</sub> O, Rhombic sulphur (SR)
6. Rhombohedral or Trigonal	$\alpha = \delta = c$ $\alpha = \beta = \gamma \neq 90^{\circ}$	Examples : CaSO <sub>4</sub> , NaNO <sub>3</sub> , KMnO <sub>4</sub>



From the above table the following points may be noted :

(i) For cubic and trigonal systems, the three edges are of equal lengths while for the remaining five systems the edges are not equal.

(ii) All the three interfacial angles are of 90° for cubic, tetragonal and orthorhombic systems while these angles for other systems are not of 90°.

### **Fourteen Bravais Lattices**

It has been shown methametically by Bravais (1848) that there are 14 independent ways of arranging the similar lattice points in a three-dimensional space, *i.e.* there are 14 space lattices in the seven systems of crystals mentioned above. These are : three cubic, two monoclinic, one triclinic, two tetragonal, four orthorhombic, one rhombohedral (trigonal) and one hexagonal as shown in Table 9.2.

Crystal system	No. of Bravais lattices	Bravais lattices	
1. Cubic	3	<ul> <li>(i) Simple cubic (sc) lattice</li> <li>(ii) Body-centred cubic (bcc) lattice</li> <li>(iii) Face-centred cubis (fcc) lattice</li> </ul>	
2. Monoclinic	2	<ul><li>(i) Simple monoclinic lattice</li><li>(ii) End-centred monoclinic lattice</li></ul>	
3. Triclinic	1	Simple triclinic lattice	
4. Tetragonal	2	<ul><li>(i) Simple tetragonal lattice</li><li>(ii) Body-centred tetragonal lattice</li></ul>	
5. Orthorhombic or Rhombic	4	<ul> <li>(i) Simple orthorhombic lattice</li> <li>(ii) Body-centred orthorhombic lattice</li> <li>(iii) Face-centred orthorhombic lattice</li> <li>(iv) End-centred orthorhombic lattice</li> </ul>	
6. Rhombohedral or Trigonal	1	Simple rhombohedral lattice	
7. Hexagonal	1	Simple hexagonal lattice	

Table 9.2. Fourteen Bravais lattices in seven systems of crystals

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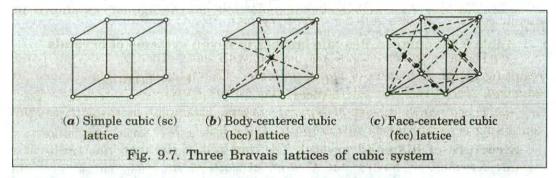
#### **Bravais Lattices of Cubic System**

Bravais lattices of the cubic system which is the simplest and also most common are considered in detail as follows. The crystals belonging to cubic system have three kinds of Bravais lattices depending on the positions of the lattice points in the unit cell of cubic system.

1. Simple cubic (sc) lattice. The unit cell of this lattice has atoms (lattice points) only at the corners of the cube [Fig. 9.7(a)]. Consequently, these atoms touch along cube edges. This structure is *loosely-packed*, since each atom has only six nearest neighbours. Only one element namely polonium exhibits this structure in a certain temperature region.

**2. Body-centred cubic (bcc) lattice.** The unit cell of this lattice has one atom at each of the eight corners and one atom at the centre of the body of the cube. [Fig. 9.7(*b*)]. The atom at the centre of the cube belongs entirely to the unit cell. The atoms are in contact along body diagonals. The elements which passess *bcc* lattice are listed below and the value of primitive, *a* (in A°) is also given in parentheses : Ba (= 5.025),  $\alpha$ -Fe (= 2.867), Rb (= 5.630), Na (= 4.291), Ti (= 3.306), W (= 3.115), U (= 3.474), Zr (= 3.620).

**3. Face-centred cubic (fcc) lattice.** The unit cell of this lattice has atoms at the six corners as well as at the centre of each of the six faces of the cube [Fig. 9.7(c)]. This structure is close-packed because each atom has 12 nearest neighbours. The atoms are in contact with the diagonal atoms. The elements which crystallise into *fcc* lattice are given below and the value of primitive a (in  $A^{\circ}$ ) is also given in parentheses : Al (= 4.049), Cu (= 3.615), Au (= 4.090),  $\gamma$ -Fe (= 3.591), Ni (= 3.524), Pt (= 4.086), Ag (= 4.086).



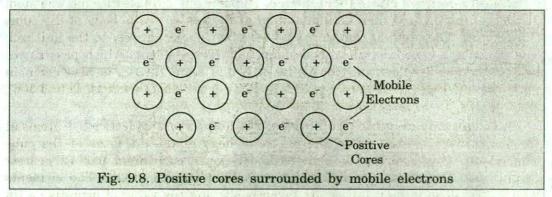
#### **Classification of Crystalline Solids or Crystals : Types of Crystals**

There are three ways to classify the crystals. But in chemistry the crystals are classified on the basis of the nature of the building particles occupying the lattice points (or lattice sites) in the crystal lattice and the nature of the bonds existing between the building particles. This basis of classification gives the following four types of crystals :

**1. Ionic crystals.** Ionic crystals are those crystals in which the particles forming the crystal are positively and negatively charged ions (*i.e.* cations and anions) which are held together by strong electrostatic force of attraction (*i.e.* by

ionic bonds). Hence the name ionic crystals. Crystals of NaCl,  $CuSO_4 \cdot 5H_2O$  etc belong to this class.

2. Metallic crystals. Metallic crystals are those in which the particles forming the crystals are metallic positive ions (called *positive cores* or *Kernels*) which are surrounded by a sea of electrons (also called electron-gas or electron-cloud) and are held together by metallic bond (Fig. 9.8). The positive metal ions are obtained when the metal atoms lose their valence-shell electrons. The electrons obtained form a sea of electrons. These electrons are not bond up with any particular metal ion and hence are free to move throughout the metallic crystal. Due to their mobile nature these electrons are called *mobile* or *delocalised electrons*. It is these mobile electrons which keep the metal positive ions held together.



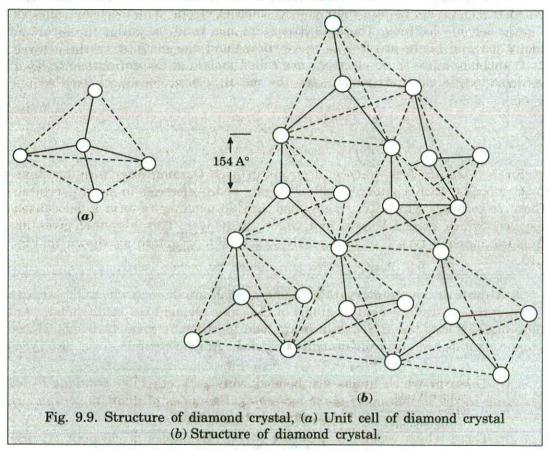
**3. Atomic or covalent crystals.** Atomic crystals are those in which the particles forming the crystal are neutral atoms of the same element (as in diamond) or of different elements (as in SiC) which are held together by covalent bonds. Hence atomic crystals are also called *covalent crystals*. Atomic crystals are of two types

(i) Those in which atoms are bonded with each other by covalent bonds resulting in the formation of giant molecules. Examples of giant molecules are diamond, silicon carbide (SiC). aluminium nitride (AlN) etc.

(*ii*) Those which consist of *separate layers*. Examples of covalent crystals containing separate layers are graphite, CdI<sub>2</sub>, CdCl<sub>2</sub>, BN etc.

Structure of diamond crystal. The unit cell of the diamond crystal is a regular tetrahedron having one C-atom at each of its four corners and one C-atom lying at its centre [Fig. 9.9 (a)]. In this unit cell, central carbon atom is linked to the four corner C-atoms by covalent bonds.

The structure of diamond is obtained by uniting a number of such unit cells in such a way that each of the four corner C-atoms of each unit cell is linked with the central C-atom of its own unit cell and with the other three corner Catoms belonging to three different unit cells [Fig. 9.9 (b)]. Thus we find that in the structure of diamond each of the C-atoms is linked with four carbon atoms. The bonds between carbon atoms are covalent bonds which run through the crystal in three dimensions. Each of the corbons in the diamond crystal is  $sp^3$ hybridised and hence each of the four covalent bonds by which each carbon is linked with the three carbons is  $sp^3(C)$ — $sp^3(C)$  o bond. The tetrahedral arrangement of four C-atoms round the central C-atom gives rise to rigid three *dimensonal network* which runs throughout the crystal. The whole lattice is, therefore, continuous and because of the continuity of C—C covalent bonding, the entire diamond crystal behaves as a single huge or giant three dimensional carbon molecule which is called **macro molecule**.



The structure of diamond discussed as above explains some of the properties of diamond as follows :

(i) High density. All the C—C bond distances are equal to 1.54 Å. This C—C bond distance is so short that high density of diamond is well explained.

(ii) Non-conductor of electricity. We have seen that, since all the four electrons present in the valence-shell of carbon atom are used up in forming four C—C  $\sigma$  bonds, no mobile electrons are left in the diamond crystal to allow the conduction of electricity. Thus diamond crystal is a non-conductor of electricity.

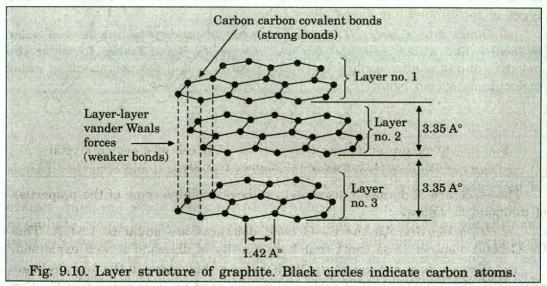
(iii) Extremely hard, high melting point and high boiling point. We have seen that, since the structure of diamond crystal consists of a large number of C—C covalent bonds, the force acting between carbon atoms is very strong and hence it is very difficult, to break these bonds. This explains the extreme hardness of diamond crystal. Also at the same time, in order to break this large number

of C-C bonds, a large amount of energy is needed. This means that diamond crystal has high melting and boiling point.

Structure of graphite. Graphite has a layer structure, *i.e.* it has a number of flat parallel layers (or planes or sheets) of carbon atoms. In each layer carbon atoms are arranged in a regular flat hexagon as in hexane, napthalene etc. C—C distance in each layer is 1.42Å which is intermediate between the single C—C bond distance (= 1.54Å) and double C=C bond distance (= 1.33Å). Note that the C=C distance in benzene compounds is 1.39Å. Each of the carbon atoms of a given layer is  $sp^2$  hybridised and is thus bonded to the adjacent three carbon atoms of the same layer by three  $sp^2(C) - sp^2(C) \sigma$ -bonds. Each of these three C—C  $\sigma$ -bonds has two-third single bond character and one-third double bond character which is due to the resonance existing between single and double bonds as shown below :

 $C = C < \begin{pmatrix} C \\ C \end{pmatrix} \leftrightarrow C - C < \begin{pmatrix} C \\ C \end{pmatrix} \leftrightarrow C - C < \begin{pmatrix} C \\ C \end{pmatrix}$ 

Since there are four valence electrons in each C-atom, after forming three C—C  $\sigma$ -bonds, each C-atom is left with one spare electron in its  $2p_z$  orbital. These  $2p_z$  orbitals which are single-filled overlap together to form a delocalised  $\pi$ -system which extends above and below each layer. This  $\pi$ -system gives an aromatic quinone type (*i.e.* hexagonal) structure to graphite as shown in Fig. 9.10.



This hexagonal structure is supported by the fact that when graphite is completely oxidised, it gives a benzene derivative *viz. mellitic acid*,  $C_6(COOH)_6$  which is benzene hexacarboxylic acid. The structure of this acid is shown in the margin. The layer structure of graphite as given above explains some of the properties of graphite as follows: СООН НООС-НООС-НООС-СООН (i) Good conductor of electricity. In each delocalised  $\pi$ -system the electrons are free to move within the layer and this accounts for the fact that graphite conducts electricity in the plane of the layer but not in the direction perpendicular to its laminal crystals. Thus graphite is a good conductor of electricity.

(*ii*) Soft, flaky and slippery substance. Every two adjacent layers in graphite are at a distance of 3.35Å. This distance is so large that the possibility of the formation of covalent bonds between the atoms of the adjacent layers is ruled out. These layers are, therefore, loosely linked together by weak Van der Waals forces. These van der Waals forces which hold the graphite crystal layers together are so weak that even a slight pressure causes the layers to slide over one another. This explains why (a) graphite is a soft substance and hence is used as a solid lubricating agent (b) graphite is flaky substance and feels slippery between the figures.

(*iii*) Black and shiny substance. The arrangement of carbon atoms in each layer causes reflection and absorption of light and hence graphite is black and shiny.

(iv) Less dense than diamond. The comparatively more open structure of graphite makes it less dense than diamond (sp. gra. of diamond = 3.52, sp. gra. of graphite = 2.25) but more reactive chemically.

4. Molecular crystals. Molecular crystals are those in which the particles forming the crystal are polar or non-polar whole molecules, except in solidified noble gases in which the particles are *atoms*, which are held together by two types of inter-molecular forces given below :

(a) Dipole-dipole forces. These forces occur in solids which consist of polar molecules like water molecules (in ice, or even in liquid state). In water the negative end of one molecule attracts the positive end of the neighbouring water molecule as shown below :

$$\overset{+}{\mathrm{H}} - \overset{-}{\mathrm{O}} \dots \overset{+}{\mathrm{H}} - \overset{-}{\mathrm{O} \dots} \overset{+}{\mathrm{H} -} \overset{-}{\mathrm{O} \dots} \overset{+}{\mathrm{H} -} \overset{-}{\mathrm{O} \dots} \overset{+}{\mathrm{O} \dots} \overset{+}{\mathrm{H} -} \overset{-}{\mathrm{O} \dots} \overset{$$

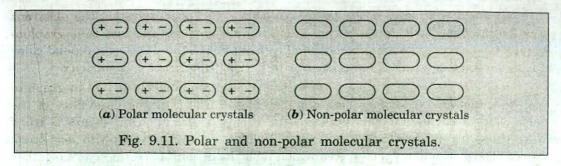
(b) van der Waals forces. These forces are more general and occur in all kinds of molecular crystals.

Both the types of inter-molecular forces mentioned above are much weaker than the electrostatic forces of attraction between cations and anions existing in ionic crystals. The binding energy in molecular crystals is, therefore, less than that in ionic crystals. The molecular crystals are of two types :

(i) Polar molecular crystals [See Fig. 9.11(a)]. Examples are water (ice) and sugar.

(ii) Non-polar molecular crystals [See Fig. 9.11(b)]. Examples are iodine, sulphur, phosphorus and solid carbon dioxide.

The polar molecular crystals are formed from unsymmetrical molecules containing polar covalent linkages and have comparatively higher melting and boiling points than the non-polar molecular crystals. This is so because in the former there are stronger dipole-dipole forces.



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### **Comparison Between Different Types of Crystals**

The comparison of properties of different types of crystals is given in Table 9.3.

## Polymorphism, Allotropy Transition Temperature, Enantiotropy and Monotropy

The phenomenon by which a substance (compound or element) exists in two or more different crystalline forms is called **polymorphism** and the different crystalline forms are said to be **polymorphous** with each other. For example  $As_2O_3$  exists in two polymorphic forms *viz. rhombic and octahedral*. These two forms are said to be polymorphous with each other. Different crystalline forms of the same element are called its **allotropes** or **allotropic forms** and the phenomenon is called **allotropy.** For example different crystalline forms of sulphur are *rhombic sulphur* or *alpha sulphur* (represented as  $S_R$  or  $S_{\alpha}$ ) and *monocilic sulphur* or *beta sulphur* (represented as  $S_M$  or  $S_{\beta}$ ).

In many cases one of the allotropic forms of a given element is stable at all the temperatures below a certain temperature which is called **transition temperature** while the other form is stable above this temperature. This phenomenon is called **enantiotropy** and the allotropic forms showing this phenomenon are called **enantiotropes** or **enantiotropic substances**. For example rhombic form of sulphur is stable at all temperatures below 96°C and above this temperature it is monoclinic form which is stable. At 96°C which is transition temperature in this ease both the forms can co-exist. The transformation of one form to the other takes place at this transition temperature and can occur in either direction. This change can be shown as :

 $S_R \rightleftharpoons^{96^{\circ}C} S_M$ 

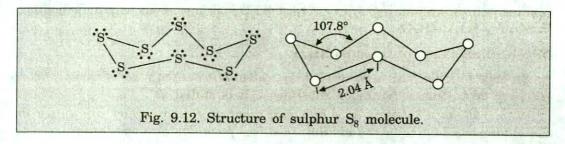
It may be noted that the transition temperature of the enantiotropes of an element is always less than the melting paint of that element. There are certain solid substances (e.g. bonzophenone and iodine chloride) whose one solid crystalline form is stable below the melting point of that substance and the other form has a metastable existence. This phenomenon is called **monotropy**. The transition temperature of the substances showing monotropy is always above their melting point.

# Table 9.3. Comparison of the properties of different types of crystals

		Different types of crystals					
	Property	Ionic crystals	Metallic crystals	Atomic or covalent crystals	Molecular crystals		
(i)	Constituent particles forming the crystal.	Positive and negative ions <i>i.e.</i> etions and anions.	Metallic positive ions surrounded by sea of electrons.	Neutral atoms	Polar or non-polar molecules		
(ii)	Forces holding the constituent particles.	Electrostatic force of attraction acting between the cations and anions.	Electrostatic force of attraction acting between metallic positive ions and sea of electrons.	Covalent bonds (Shared pairs of electrons).	Weak polar forces in polar molecular crystals, van der Waals forces in non-polar molecular crystals.		
(iii)	Hardness	Hard and brittle.	Usually hard.	Usually very hard.	Polar molecular crystals are moderately hard and non-polar molecular crystals are very soft.		
(iv)	Solubility	Soluble in polar solvents.	Dissolve in solvents by chemical action.	Insoluble in most solvents.	Polar molecular crystals ale usually soluble in polar solvents while non-polar molecular crystals are usually soluble in non-polar solvents.		
(v)	Melting and boiling points.	High	High	Very high	Low		
(vi)	Electrical conductivity.	High in fused state.	High	Usually low	Extremely low.		
(vii)	Examples	NaCl	Cu metal	Diamond, graphite	Ice (polar molecular crystal), solid carbon dioxide (non-polar molecular crystal).		

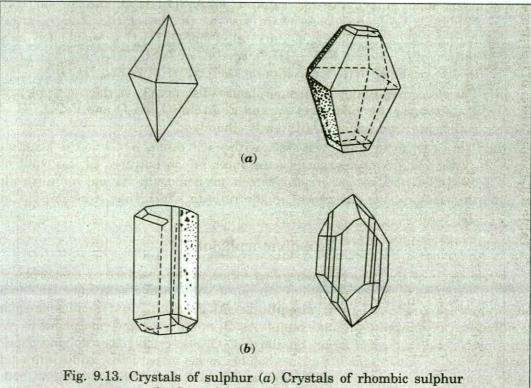
#### Allotropic Forms of Sulphur

Sulphur exists in two crystalline forms : (i) Rhombic or octohedral or alpha sulphur (ii) Monoclinic or prismatic or beta sulphur. Both the forms are found to exist in octaatomic crystals in the form of a puckered ring, i.e. in both the forms sulphur exists in the form of octagonal ring molecules ( $S_8$  molecules) in which the eight sulphur atoms are joined by covalent bonds (Fig. 9.12).



Such rings give molecular crystal in which the rings are held together by relatively weak polar forces. Consequently both the forms have low melting points.

Rhombic sulphur has octahedral shape while monoclinic sulphur has long needle like shape (Fig. 9.13).



(b) Crystals of monoclinic sulphur.

# Isomorphism

When two or more crystalline substances have the same number of atoms and the same shape (*i.e.* the atoms in them are united in a similar manner), the phenomenon is called **isomorphism** and such substances are said to be **isomorphous** substances with each other. (*Isomorphous* = having the same shape). For example  $ZnSO_4$ .  $7H_2O$  and  $FeSO_4$ .  $7H_2O$  are isomorphous with each other. Similarly chrome alum,  $K_2SO_4$ .  $Cr_2(SO_4)_3$ .24 $H_2O$  is isomorphous with potash alum,  $K_2SO_4$ .  $Al_2(SO_4)$ .24 $H_2O$ .

## Mitcherlich's Law of Isomorphism

In 1820 Mitcherlich put forward a law, called *Mitcherlich's law of isomorphism* with regard to the isomorphous substances. It is stated as :

Isomorphous substances have an equal number of atoms which are united in a similar way, i.e. they have similar chemical formulae or constitution.

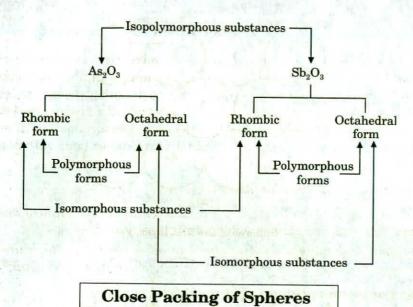
#### Properties of Isomorphous Substances

The chief characteristics of isomorphous substances are :

- (i) The crystals of these substances have the same shape.
- (*ii*) The crystals of one substance can be grown in a saturated solution of the other isomorphous substance. For example, if a crystal of  $FeSO_4.7H_2O$  is suspended in a saturated solution of  $ZnSO_4.7H_2O$ , the former (*i.e.*  $FeSO_4.7H_2O$ ) begins to grow in size as the latter (*i.e.*  $ZnSO_4.7H_2O$ ) deposits on it. Similarly, if a crystal of  $ZnSO_4.7H_2O$  is suspended in a saturated solution of  $FeSO_4.7H_2O$ , crystals of  $ZnSO_4.7H_2O$  begin to grow in size as  $FeSO_4.7H_2O$  begins to grow in the crystal of  $ZnSO_4.7H_2O$ .
- (*iii*) The elements forming the isomorphous substances have the same valency. For example the valency of Zn and Fe in  $ZnSO_4.7H_2O$  and  $FeSO_4.7H_2O$  which are isomorphous with each other is 2.
- (iv) They can form mixed crystals with each other, *i.e.* when a solution containing two isomorphous substances is concentrated to the point of crystallisation, we get crystals which are homogeneous and contain both the isomorphous substances in the ratio in which they were present in the solution.

# Isopolymorphism

When each of the two polymorphous forms of a substance is isomorphous with each of the two polymorphous forms of some other substance, the two substances are said to be **isopolymorphous** with each other and the phenomenon is called **isopolymorphism**. For example  $As_2O_3$  exists in two polymorphous forms *viz. rhombic* and *octahedral* forms. Similarly  $Sb_2O_3$  also exists in two polymorphous forms *is chombic* and *octahedral*. The rhombic forms of both the oxides are said to be isomorphous with each other and so are said the octhedral forms of both the oxides. Consequently both the oxides are isopolymorphous with each other. This is shown below :



It has been observed that the structures of most of the crystals studied in inorganic chemistry is obtained by the most efficient packing of the units of which these crystals are composed. These units may be either atoms, ions or molecules which are of approximately spherical shape, having equal size. It is, therefore, essential to study the ways in which these units are packed together in three dimensions.

Place some solid spheres of equal size in one row on the table. Place another row of the spheres in such a manner that the spheres of the second row rest between the depressions of every two spheres of the first now. In this way place some rows of the spheres as shown in Fig. 9.14(a) in which three rows of spheres have been shown. The spheres of this layer have been represented by full line circles.

The following points may be noted from Fig. 9.14(a).

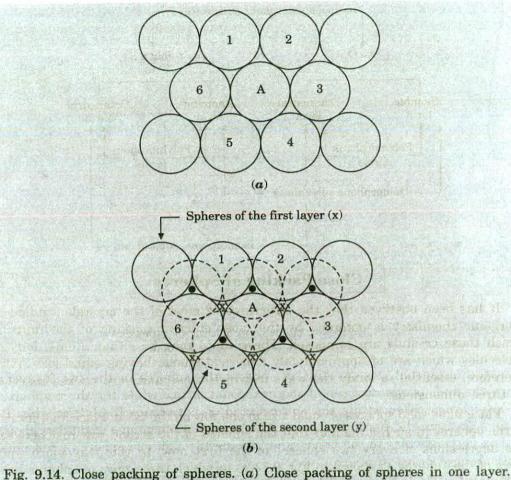
(i) Every sphere is surrounded by six other similar spheres. For example the sphere marked with A is surrounded by six other similar spheres marked as 1, 2, 3, 4, 5 and 6. Thus we see that every sphere has 6 nearest neighbours. The number of nearest neighbours is called the **coordination number** (C. N.). Thus the C. N. of each of the spheres arranged in this manner is six. It has been shown by calculation that in this arrangement only 60.4% of the space is occupied by the spheres while the remaining 39.6% of the space remains unoccupied (vacant). This vacant space is called **void volume**.

(*ii*) There is an opening between each set of three touching spheres. These openings have been represented as  $\bullet$  and  $\times$ .

Now place a second layer of spheres (shown by dotted line spheres) on the spheres of the first layer so that the openings shown as  $\bullet$  are covered by them while those shown as  $\times$  remain uncovered [Fig. 9.14 (b)].

Now suppose we have to build up a third layer of spheres over the second layer. It can be done in any of the following two ways :

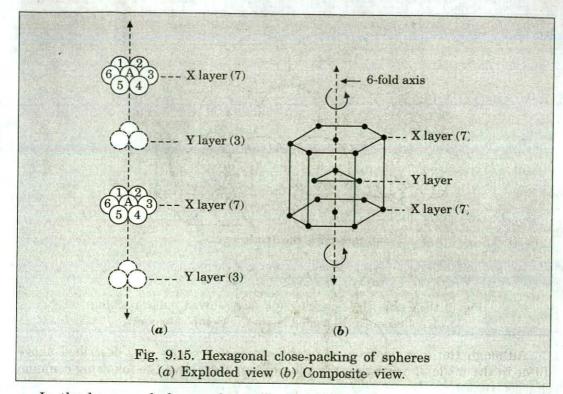
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(b) Close packing of spheres in two layers.

First way. In this way, the spheres of 3rd layer (not shown in the Figure) are placed so that the centres of the spheres of the 3rd layer are directly above the centres of the spheres of the first layer. Thus in this arrangement the spheres of the first layer and those of the third layer are exactly identical. This arrangement of close-packing of spheres is referred to as X Y X arrangement of spheres where X, Y and X represent the 1st, 2nd and 3rd layers of spheres. Quite obviously 1st and 3rd layers are identical.

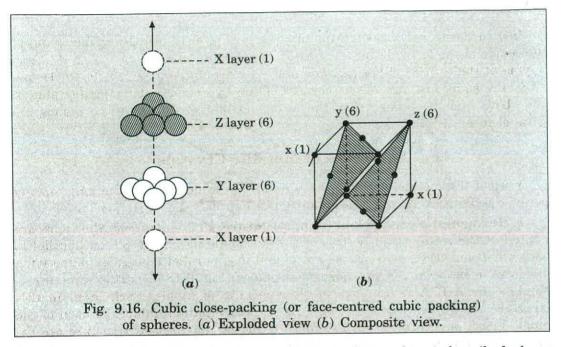
When X Y X Y X Y ... arrangement of packing of spheres is continued indefinitely, the system obtained is found to possess *hexagonal symmetry* (This system should not be confused with the hexagonal pattern of spheres), *i.e.* this system possesses one 6-fold axis of symmetry which is perpendicular to the planes of the close- packed spheres. Such as arrangement of three dimensional packing of spheres is shown in Fig. 9.15. Because of its hexagonal symmetry this arrangement is called **hexagonal close-packing** of spheres and is abbreviated as **hcp.** 



In the hexagonal close-packing of spheres the spheres in the two X-layers occupy the sites of the unit cell of the hexagonal lattice while the three spheres of Y-layer are situated within the unit cell and do not occupy the lattice sites. It can be seen from the figure that when the hexagonal structure is rotated about the axis perpendicular to the layers and passing through one sphere, it presents identical view thrice in one rotation.

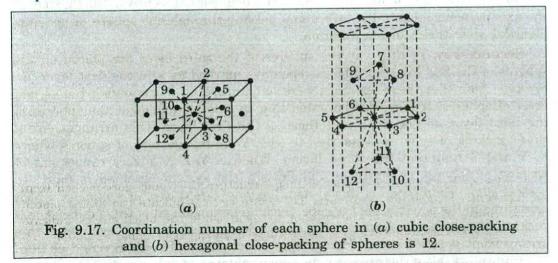
Second way. In this way the spheres of the third layer are placed on the spheres of the 2nd layer so that the openings marked as  $\times$  in the first layer are covered. Note that these openings were left uncovered in arranging the second layer of spheres. It may also be noted that in this arrangement the spheres of the third layer do not come over those of the first layer. This arrangement of close- packing of spheres is referred to as X Y Z arrangement of spheres where X, Y and Z represent the three layers. When X Y Z X Y Z ... arrangement of packing of spheres is continued indefinitely, the system obtained is found to possess cubic symmetry, i.e. this system has four 3-fold axes of symmetry which pass through the diagonals of the cube. Such an arrangement of three dimensional packing of spheres is shown in Fig. 9.16. Because of its cubic symmetry this arrangement is called *cubic close-packing* of spheres and is abbreviated as ccp. The unit cell of this structure is a cube which contains 14 spheres. An examination of the arrangement of 14 spheres in the unit cell of ccp structure reveals that this structure has one sphere at the centre of each of the six faces of the unit cell. It is for this reason that ccp structure is also sometimes called face-centred cubic (fcc) structure.

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Although the two closest packing of spheres (hcp and ccp) described above differ in the mode of arranging the spheres, yet they have the following common characteristics :

(i) In both the packings of spheres, each sphere is surrounded by 12 other equidistant spheres, *i.e.* coordination number of each sphere in both the packings of spheres is 12. This fact has been illustrated in Fig. 9.17 (a) and (b).



(ii) In cubic close-packing of spheres [Fig. 9.17 (a)] the sphere lying at the centre of the middle face has four nearest neighbours marked as 1, 2, 3 and 4 lying at the corners of that face and eight more marked as 5, 6, 7, 8, 9, 10, 11 and 12 at the same distance at the centres of four faces of adjoining cubes.

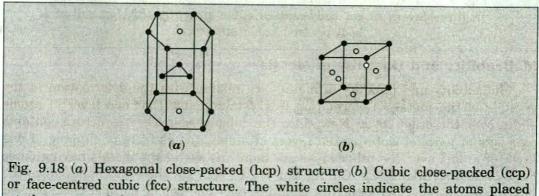
(iii) In hexagonal close-packing of spheres [Fig. 9.17 (b)] the sphere lying at the centre of the hexagon has six nearest neighbours marked as 1, 2, 3, 4, 5 and 6 lying at the corners of the hexagon and six more marked as 7, 8, 9, 10, 11 and 12 at the same distance at the corners of the two adjascent triangular planes, one above and the other below the hexagonal plane. All the three planes are parallel to each other.

## **Structure of Metallic Crystals**

Most of the metals belonging to s- and d-block elements of the long form of periodic table have any of the following structures.

1. Hexagonal close-packed (hcp) structure. In this structure the atoms are located at the corners and centres of two hexagons which are placed parallel to each other and three more atoms are placed in a parallel triangular plane lying mid way in between the two hexagonal planes [Fig. 9.18 (a)]. This structure is obtained by A B A B A... type of close-packing of atoms. Each atom in this structure has 12 nearest neighbours, *i.e.* the coordination number of each of the atoms in *hcp* structure is 12. Examples of metals having *hcp* structure are Cr, Mo, V, Mg, Zn etc.

2. Cubic close-packed (ccp) or face-centred cubic (fcc) structure. In this structure the atoms are located at the corners and at the centres of all the six faces of a cube (Fig. 9.18 (b)). This structure is obtained by ABC ABC type of close-packing of atoms. Each atom in this structure has 12 nearest neighbours, *i.e.* coordination number of each atom in this structure is 12 as already discussed. Examples of metals having *ccp* or *fcc* structure are Cu, Ag, Au, Ni, Pt etc.



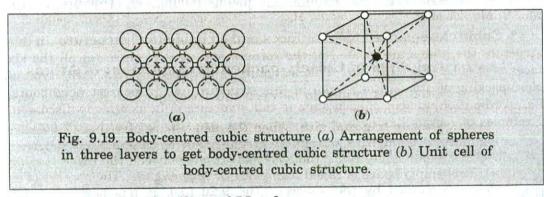
or face-centred cubic (fcc) structure. The white circles indicate the atoms placed at the centre of the face of the cube or hexagon while the black circles indicate the atoms lying at the corners of hexagon or cube.

**3. Body-centred cubic (bcc) structure.** In this structure the atoms are not closely packed as in the above two structures. This structure is obtained by the following two steps :

(i) Place some spheres (represented by full line circles) side by side so that they are slightly opened up. By doing so none of the spheres touches each other [See Fig. 9.19 (a)].

(ii) Place the second layer of spheres (represented by clotted line) on the openings between the spheres of the first layer so that each sphere of the 2nd layer is in contact with four spheres of the first layer.

(*iii*) Now place a third layer of spheres so that the openings in the second layer (marked as  $\times$ ) are covered by them. Thus we see that third layer is exactly identical to first layer. This type of arrangement of spheres gives *body-centred cubic* (*bcc*) structure in which each of the spheres (or atoms) is attached with eight nearest spheres (four spheres in the layer just above and four spheres in the layer just below) and so the *coordination number in body-centred cubic structure is only eight*. It is for this reason that the atoms in this structure are not closely packed, and only 68% of the total volume is actually occupied by the atoms. However, the atoms are in close contact along body diagonals. The unit cell of this structure has one atom at each corner and one atom at the centre of the cube [Fig. 9.19 (b)]. Alkali metals have body centred cubic structure.



## **Malleability and Ductility of Metals**

• Malleability and ductility of metals are related with the deformation in the crystals of the metals. Deformation in crystals means that one layer of atoms slides over the other layer. Now since the cubic close-packed structure contains *four* sets of parallel close-packed layers of atoms, the chances of slipping of one layer of atoms over the other layer are more in case of the metals having cubic close-packed structure (*e.g.* Cu, Ag, Au, Ni, Pt etc.) On the other hand, since the hexagonal close-packed structure contains only *one* set of parallel close-packed layer of atoms, the chances of slipping of one layer of atoms over the other layer are very little in case of metals having hexagonal structure (*e.g.* Cr, Mo, V, Mg, Zn etc.). From the above discussion it can be concluded that the metals like Cu, Ag, Au, Ni, Pt etc which have cubic close-packed structure are more malleable (*i.e.* can be beaten into sheets) and ductila (*i.e.* can be drawn into wires) than the metals like Cr, Mo, V, Mg, Zn etc which have hexagonal close-packed structure.

Since Fe can adopt both these structures depending on temperature, this metal shows a wide variety of properties.

## Characteristics of hcp, ccp and bcc Structures

The characteristics of *hcp*, *ccp* and *bcc* structures mentioned above have been summarised in Table 9.4.

			Structure		
de la composición de la compos	Characteristics	Hexagonal close- packed (hcp)	Cubic close packed (ccp)	Body centred cubic (bcc)	
1,	Nature of packing of atoms	Close-packed	Close-packed	Not close-packed	
2.	Volume occupied by atoms	74% of the total volume	74% of the total volume	68% of the total volume	
3.	Type of packing of atoms	ABABABA	ABCABC	and the second sec	
4.	Coordination number	12	12	8	
5.	Malleability and ductility	Less malleable and ductile	More malleable and ductile	Malleable and ductile	
6.	Examples of metals	Cr, Mo, V, Mg, Zn etc.	Cu, Ag, Au, Ni, Pt etc.	Alkali metals.	

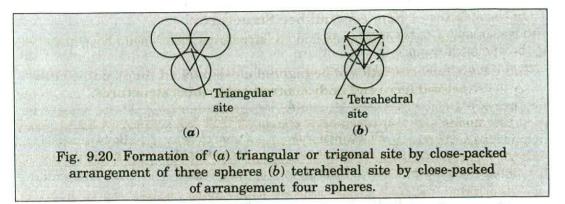
Table 9.4. Characteristics of hexagonal close-packed (hcp), cubic closepacked (ccp) and body centred-cubic (bcc) structures.

# **Interstitial Sites in Closely-packed Arrangement of Atoms**

The interstitial sites formed in between the closely-packed atoms of a given crystal are of the following types :

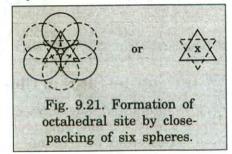
1. Triangular or trigonal site. When the spheres are placed at the vertices of an equilateral triangle, a triangular arrangement of close-packed spheres is obtained and some empty space (hole or void) is left between the three touching spheres. This empty space is called *triangular or trigonal site*. The corners of the triangle are occupied by the spheres [Fig. 9.20 ( $\alpha$ )]. It has been shown by calculations that the radius of the sphere which can fit into the trigonal site without disturbing the close-packed arrangement of the surrounding large spheres should not be greater than 0.155 times that of the surrounding large close-packed spheres.

2. Tetrahedral site. When a sphere is placed on the three spheres placed at the vertices of an equilateral triangle and touching each other, a tetrahedral arrangement of close-packed spheres is obtained. In this arragement the centres of the four spheres lie at the apices of a regular tetrahedron [Fig. 9.20 (b)]. The empty space left at the centre of this tetrahedron is called *tetrahedral site*. It may be mentioned here that it is not the shape of the void which is tetrahedral but it is the arrangement of the spheres which is tetrahedral. In a close-packed arrangement of spheres, each sphere is in contact with three spheres in the layer above it and other spheres in the layer below it. Thus there are two tetrahedral sites associated with each sphere. The size of the tetrahedral site is much smaller than the size of the sphere. With the increase of the size of the spheres, the size of the tetrahedral site also increases. Calculations have shown that a tetrahedral site can accomodate a sphere whose radius should not be greater than 0.225 times that of the spheres forming the tetrahedral site.



3. Octahedral site. This interstitial site is formed by joining six spheres whose centres lie at the apices of a regular octahedron as shown in Fig. 9.21. This site is found in both hcp and ccp systems. Fig. 9.21 shows that an octahedral site is generated by two equilateral triangles whose apices point in opposite directions. One of these triangles joins the centres of three spheres in one plane while the other triangle (shown by dotted lines) joins the centres of the three

spheres (shown by dotted lines) in the second plane. The octahedral site marked as  $\times$  is formed where two triangles of spheres belonging to different layers are super-imposed on each other. It may also be noted that there is only one octahedral site for each sphere. Thus the number of octahedral sites is half the number of tetrahedral sites. The sizes of different sites studied so far are related as :



octahedral site > tetrahedral site < trigonal site.

Calculations have shown that an octahedral site can accomodate a sphere whose radius should not be greater than 0.414 times that of the spheres forming octahedral site.

# Radius Ratio Rule and its Effect on the Shape of Ionic Crystals.

The ratio of the radii of the positive and negative ions is called the radius ratio. Thus :

Duding	ratio =	Radius of positive ion (cati			(cation)	
nuuus	1000 -	Radius	of	negative	ion	(anion)

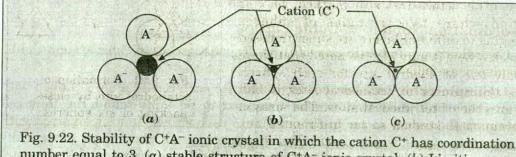
The effect of radius ratio in determining the coordination number and the shape of the ionic crystals is known as *radius ratio effect*. The radius ratio can be used in determining the most stable form of arrangement of ions in the crystal lattice of an ionic solid.

In order to understand the application of radius ratio concept, let us suppose that the coordination number of a cation C<sup>+</sup>, in an ionic crystal, C<sup>+</sup>A<sup>-</sup> is 3. Thus three A<sup>-</sup> anions are in contact with one C<sup>+</sup> ion [Fig. 9.22 (a)].

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In the structure shown in Fig. 9.22(*a*), since the cation  $(C^+)$  is in close contact with the anions  $(A^-)$ , the force of attraction between  $C^+$  and  $A^-$  ions is quite strong. At the same time, since the anions are not at all in contact with each other, the force of repulsion between them is quite small. Thus this structure is quite stable.

In the structure shown in Fig. 9.22(b), since the cation is touching the anions, the force of attraction between C<sup>+</sup> and A<sup>-</sup> ions is quite strong. At the same time, since the anions are also touching one another, the force of repulsion between them is also quite strong. Thus this structure is a limiting case of stable structure of C<sup>+</sup>A<sup>-</sup> ionic crystal. It can be shown by simple calculation that in this structure the radius ratio,  $r(C^+)/r(A^-) = 0.155$ . If the value of radius ratio,  $r(C^+)/r(A^-)$  falls below this value (*i.e.* if C<sup>+</sup> cation becomes still smaller in size), the structure of C<sup>+</sup>A<sup>-</sup> ionic crystal will become unstable and will be as shown in Fig. 9.22 (c). In the structure shown at (c), since the cation is not touching the anions, the force of attraction between C<sup>+</sup> and A<sup>-</sup> is weak. At the same time, since the anions are still touching each other, the force of repulsion between them is strong. Thus this structure is unstable and cannot exist. The above discussion makes it evident that for coordination number of 3, the limiting radius ratio value  $r(C^+)/r(A^-) = 0.155$ .



number equal to 3. (a) stable structure of  $C^+A^-$  ionic crystal. (b) Limiting case of stable structure of  $C^+A^-$  ionic crystal with  $r(C^+)/r(A^-) = 0.155$ . (c) Unstable structure of  $C^+A^-$  ionic crystal.

By applying simple geometry in the same way, the limiting radius ratio values for various maximum coordination numbers of the cation can be calculated. These values and the shapes of the ionic crystals resulted from various coordination numbers are given in Table 9.5.

Radius ratio, [r(C <sup>+</sup> )/r(A <sup>-</sup> )] value	Maximum coordination number of cation	Arrangement of anions round the cation	Examples
0 to 0.155	2	Linear	
0.155 to 0.225	3	Trigonal planar	B <sub>2</sub> O <sub>3</sub>
0.225 to 0.414	4	Tetrahedral	ZnS
0.414 to 0.732	6	Octahedral	NaCl
0.732 to 1.000	8	Body-centered cubic	CsCl

Table 9.5. Radius	ratio values for different coordination	
and the second second second	numbers of a cation.	

## What is Co-ordination Number of an Ion ?

For maximum stability of an ionic crystal, the arrangement of different ions in an ionic crystal should be such that the forces of attraction between cations and anions are maximum and those of repulsion between cations or anions are minimum. Thus for maximum stability of an ionic crystal, the ions having similar charges should be close to one another and those having opposite charges should lie away from one another. Therefore, in order to realise this condition of stability, each ion is surrounded by the greatest possible numer of ions having opposite charges. The number of oppossitely charged ions surrounding any particular ion (which may be a cation or an anion) in the unit cell of the crystal structure is called the co-ordination number of that particular ion. This is denoted by C.N.

In ionic crystals of  $A^+B^-$  type (e.g. NaCl, ZnS etc.) since each ion is surrounded by the same number of oppositely charged ions, the C.N. of the cation (A<sup>+</sup>) is the same as that of the anion (B<sup>-</sup>). But in case of ionic crystals of  $A^{2+}B_2^{-}$ , (e.g. CaF<sub>2</sub>) or  $A_2^+B^{2-}$  (e.g. Na<sub>2</sub>S), the C.N. of the cation ( $A^{2+}$  or  $A^+$ ) is different from that of the anion (B<sup>-</sup> or B<sup>2-</sup>), since the number of each kind of ions is not the same as in case of ionic crystals of  $A^+B^-$  type. For example in CaF<sub>2</sub> ionic crystal, each of the Ca<sup>2+</sup> ions is surrounded by eight F<sup>-</sup> ions and each of the F<sup>-</sup> ions is surrounded by four Ca<sup>2+</sup> ions. Thus the C.N. of Ca<sup>2+</sup> and F<sup>-</sup> ions is 8 and 4 respectively.

# **Co-ordination Number of Cubic Lattice**

Co-ordination number in case of three Bravais lattices of cubic system can be considered as follows :

1. Simple cubic (sc) lattice. In this lattice each corner atom is linked with seven other unit cells that can be imagined to be built round the unit cell containing the corner atom. In this structure each corner atom is adjoined with other atoms out of which four atoms are in the same plane, one is vertically above it and the other is immediately below it. Thus each atom in this structure has a total of *six nearest* neighbouring atoms and hence the co-ordination number for this lattice is *six*.

2. Body centred cubic (bcc) lattice. In this structure the nearest neighbours of any corner atom are the body-centred atoms and not the other corner atoms. Since each corner atom is linked with eight unit cells, the eight body-centred atoms form the *nearest* neighbours for any corner atom. Consequently the coordination number of this structure is *eight*.

**3. Face-centred cubic (fcc) lattice.** In this structure the nearest neighbours of any corner atom are the face-centred atoms of the surrounding unit cells. Any corner atom has four such atoms in its own plane, four in a plane above it and four in a plane below it. Thus the co-ordination number of this structure is *twelve*.

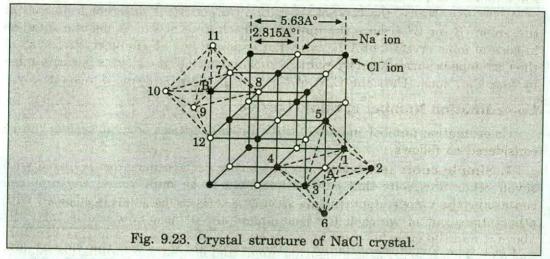
## Structures of Ionic Crystals of AB Type

Here we shall discuss the structures of NaCl, CsCl and ZnS which are the representatives of the three common structural arrangements by which similar compounds are expressed.

**1. NaCl crystal (6 : 6 co-ordination crystal).** A unit cell representation of NaCl ionic crystal is shown in Fig. 9.23. The salient features of this structure are summarised below :

(i)  $Cl^-$  ions have cubic close packed arrangement in which all the octahedral holes are filled by Na<sup>+</sup> ions.

(*ii*) In this ionic crystal, the radius ratio,  $r(Na^+)/r(Cl^-) = 0.95/1.81 = 0.524$ . Since this value lies between 0.414 and 0.732, the co-ordination number of each of the ions is *six*, *i.e.* each Na<sup>+</sup> ion is surrounded by *six* Cl<sup>-</sup> ions and similarly each Cl<sup>-</sup> ion is surrounded by *six* Na<sup>+</sup> ions which are placed at the six corners of a regular octahedron. Thus we may say that this structure has 6 : 6 coordination. The octahedral arrangement of six Cl<sup>-</sup> ions marked 1, 2, 3, 4, 5, 6 round one Na<sup>+</sup> ion marked as 7, 8, 9, 10, 11, 12 round one Cl<sup>-</sup> ion marked as B has been shown in Fig. 9.23.



An examination of the cubical structure of NaCl crystal as shown in Fig. 9.23 makes it clear that the distance between two adjascent ions of the same kind like, say Cl<sup>-</sup> ions (*i.e.* length of the edge) is equal to 5.63 Å while the distance between two adjacent ions of different kind like, say Na<sup>+</sup> and Cl<sup>-</sup> ions, is equal to 5.63/2 = 2.815 Å.

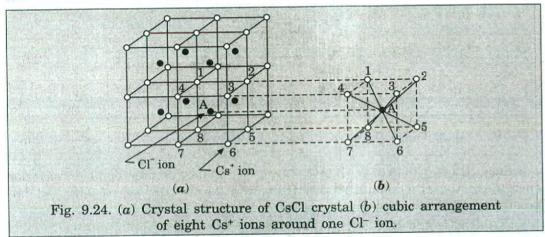
It is worth noting that  $Na^+$  and  $Cl^-$  ions are not connected to one another by pairs, since all the six  $Cl^-$  ions are the same distance away from any one  $Na^+$  ion. Thus for the maximum stability of NaCl crystal the oppositely charged ions are close to one another and the similarly charged ions are as away from one another as possible.

Although discrete molecules (Na<sup>+</sup>Cl<sup>-</sup>) do not exist in the solid form of ionic crystals, independent molecules do exit in the vapour form of ionic compounds.

Examples of some other compounds which have NaCl structures are : NaI, KCl, RbI and RbF.

2. CsCl crystal (8:8 co-ordination crystal). The structure of CsCl is shown in Fig. 9.24. The salient features of this structure are summarised below: (i) In this structure, the radius ratio,  $r(Cs^+)/r$  (Cl<sup>-</sup>) = 1.69/1.81 = 9.33 Since this value lies between 0.732 and 1.000, the co-ordination number of the ions is 8, *i.e.* each Cs<sup>+</sup> ion is surrounded by eight Cl<sup>-</sup> ions and similarly each Cl<sup>-</sup> ion is surrounded by eight Na<sup>+</sup> ions. Thus we can say that this structure has 8 : 8 co-ordination.

(*ii*) The arrangement of the ions in this crystal is body-centred cubic, *i.e.* the unit cell of its structure has one ion at the centre and the oppositely-charged ions at the corner of the cube. The cubic arrangement of eight Cs<sup>+</sup> ions round one Cl<sup>-</sup> ion marked as A has been shown in Fig. 9.24 (*b*). Here it should be noted that the arrangement of the ions in this crystal is not strictly body-centred cubic, since in a body-centred cubic arrangement the atom/ion at the centre and those at the corners of the cube are identical whereas in CsCl crystal these atoms or ions are different as mentioned above.



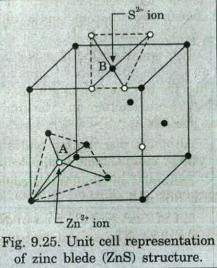
CsCl type structure is found in those crystals in which the cations are comparable in size to anions.

Examples of some other compounds which have CsCl structure are CsBr, CaI, TlCl, TlBr and TlI.

3. Zinc blende (ZnS) crystal (4 : 4 coordination crystal). A unit cell representation of the structure of this crystal is shown in Fig. 9.25. The important characteristics of this structure are :

(i)  $S^{2-}$  ions are in the cubic close-packed arrangement, *i.e.*  $S^{2-}$  ions are placed at the corners and at the centre of each face of the cube.

(*ii*) The co-ordination number of each ion is 4, *i.e.* each  $Zn^{2+}$  ion is tetrahedrally surrounded by four  $S^{2-}$  ions and similarly each  $S^{2-}$  ion is tetrahedrally surrounded by four  $Zn^{2+}$  ions. The tetrahedral arrangement of four



 $S^{2-}$  ions round one  $Zn^{2+}$  ion marked as A and the tetrahedral arrangement of four  $Zn^{2+}$  ions round one  $S^{2-}$  ion marked as B has been shown in Fig. 9.25. Thus zinc blende is 4 : 4 co-ordination compound.

Examples of some other compounds which have zinc blende structure are : CuCl, CuBr, CuI, AgI and BeS.

4. Wurtzite (ZnS) cystal (4 : 4 coordination crystal). A unit cell representation of the structure of this crystal is shown in Fig. 9.26. The important characteristics of this structure are :

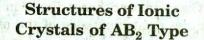
(i)  $S^{2-}$  ions are in the hexagonal closepacked arrangment.

(ii) The coordination number of each ion is 4, *i.e.* each  $Zn^{2+}$  ion is tetrahedrally surrounded by four S<sup>2-</sup> ions and similarly each S<sup>2-</sup> ion is tetrahedrally surrounded by four Zn<sup>2+</sup> ions. The tetrahedral arrangement of four S<sup>2-</sup> ions around one Zn<sup>2+</sup> ion marked as A and the tetrahedral atrangement of four Zn<sup>2+</sup> ions round one S<sup>2-</sup> ion marked as B has been shown in Fig. 9.26. Thus wurtzite is 4 : 4 coordination compound.

Other compounds having wurtzite structure are : ZnO, CdS and BeO.

The structures of zinc blende and wurtzite as described above show that they are very similar to each other. The only difference is in the arrangement

of close-packed layers of S2- ions. In zinc blends S2- ions have cubic closepacked arrangement while in wurtzite the same ions have hexagonal closepacked arrangement.



Here we shall discuss the structures of fluorite (CaF2) and rutile  $(TiO_2)$  which are the representatives of the structural arrangements by which similar compounds are expressed.

1. Fluorite, (CaF<sub>2</sub>) crystal (8:4 coordination crystal). The unit cell representation of the structure of CaFo crystal is shown in Fig. 9.27. The important points are :

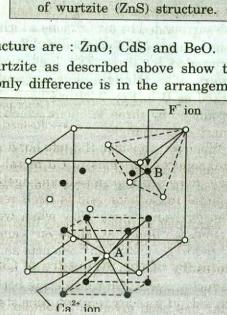
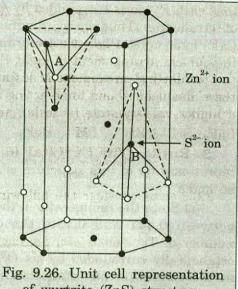


Fig. 9.27. Unit cell representation of fluorite. (CaF2) structure. The cubical arrangement of eight  $F^-$  ions around one Ca2+ ion and tetrahedral arrangement of four Ca2+ ions around one F- ion have also been shown.



of wurtzite (ZnS) structure.

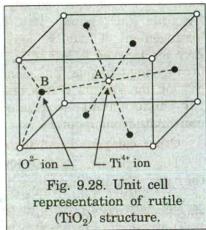
(i)  $Ca^{2+}$  ions are in cubic close-packed arrangement, *i.e.*  $Ca^{2+}$  ions occupy all the corners and central positions of each face of the cube.

(*ii*) Since the radius ratio value of this crystal is 0.73, the coordination number of  $Ca^{2+}$  ion is 8, *i.e.* each  $Ca^{2+}$  ion is surrounded by eight F<sup>-</sup> ions which are placed at the corners of a cube. F<sup>-</sup> ions are so placed at the corners of a cube that each F<sup>-</sup> ion is surrounded by *four*  $Ca^{2+}$  ions which are placed at the vertices of tetrahedron. Thus the coordination number of each F<sup>-</sup> ion is 4 and consequently  $CaF_2$  ionic crystal has 8 : 4 coordination. For the sake of better understanding the cubical arrangement of eight F<sup>-</sup> ions around one  $Ca^{2+}$  ion marked as A and the tetrahedral arrangement of four  $Ca^{2-}$  ions around one F<sup>-</sup> ion marked as B have also been shown in Fig. 9.27.

Other examples of crystals having fluorite type crystal structure are  $SrF_2$ ,  $BaF_2$ ,  $SrCl_2$ ,  $BaCl_2$ ,  $CdF_2$ ,  $HgF_2$ .

2. Rutile  $(TiO_2)$  crystal (6 : 3 coordination crystal). The unit cell representation of this structure is shown in Fig 9.28. The following points may be noted :

(i) Since the radius ratio in this crystal lies between 0.441 and 0.732, the coordination number of Ti<sup>4+</sup> ion is six, i.e. each Ti<sup>4+</sup> ion is octahedrally surrounded by six O<sup>2-</sup> ions placed at the corners of an octahedron. For example Ti<sup>4+</sup> ion marked as A in Fig. 9.28 has been shown to be surrounded by six O<sup>2-</sup> ions which are placed at the corners of an octahedron. Each O<sup>2-</sup> ion is surrounded by three Ti<sup>4+</sup> ions placed at the corners of a triangle. For example O<sup>2-</sup> ion marked as B in Fig. 9.28 has been shown to be surrounded by three Ti<sup>4+</sup> ions which occupy the corners of a triangle.



(ii) Ti<sup>4+</sup> ions have sufficiently distorted body-centred cubic arrangement. The distortion in the body-centred cube is because of the fact that one of the sides of the cube is shorter than the other sides. Thus we see that TiO<sub>2</sub> is not exactly close-packed structure.

Examples of other crystals having  $TiO_2$  type structure are  $NiF_2$ ,  $CoF_2$ ,  $MnF_2$ ,  $MgF_2$ ,  $ZnF_2$ ,  $FeF_2$ ,  $SnO_2$ ,  $PbO_2$ ,  $MnO_2$ .

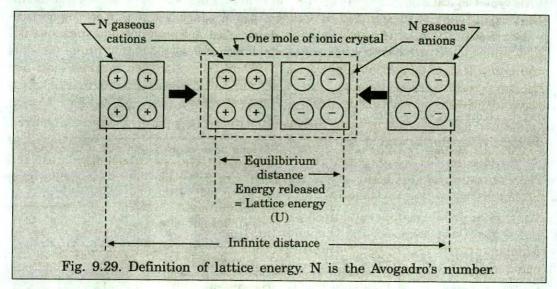
# Summary of the Structure of Common Ionic Crystals

The summary of the structure of common ionic crystals that we have studied so far has been given in a tabular form in Table 9.6.

## Lattice Energy of Ionic Crystals

The stability of an ionic crystal is measured in terms of its lattice energy which is defined as follows :

Lattice energy of an ionic crystal is defined as the energy released when a mole of gaseous cations (i.e. N gaseous cations where N is Avogadro's number) and a mole of gaseous anions (i.e. N gaseous anions) separated from each other by an infinite distance are brought to their equilibrium distance to form one mole of the ionic crystal (See Fig. 9.29).



The formation of a mole of an ionic solid,  $A^+B^-(s)$  from its constituent gaseous ions,  $A^+(g)$  and  $B^-(g)$  may be represented by the equation :

 $A^+(g) + B^-(g) \rightarrow A^+B^-(s) + Energy released (called lattice energy).$ 

one mole of ionic solid

At equilibrium distance the ionic crystal has the *lowest energy* and hence is in the *most stable state* at this distance.

Lattice energy can also be defined as :

Lattice energy is the energy required to move the ions of one mole of an ionic crystal separated from each other by an equilibrium distance to an infinite distance. In simple words lattice energy of an ionic crystal,  $A^+B^-(s)$  is numerically equal to that which is required to convert one mole of the same ionic solid into its constituent gaseous ions, *i.e.* 

Lattice energy is presented by U. It is generally represented by placing a negative sign before its value. Negative sign indicates that the formation of an ionic solid from its gaseous cations and anions is an *exothermic process*, *i.e.*, in the formation of the ionic solid there is a release of energy and hence the energy of the system is decreased. This is because of the decrease in energy that the ionic solid is more stable than the individual ions of which the ionic solid is composed.

Greater is the value of lattice energy of an ionic solid, more stable is the ionic solid.

Crystal	Coordination number of each ion	Nature of arrangement of ions	Examples
AB type Crystal		and the second second second	
(1) Rock salt (NaCl)	Na <sup>+</sup> = 6 Cl <sup>-</sup> = 6 Both octahedral	Cl <sup>-</sup> ions have cubic close-packed arrange- ment with Na <sup>+</sup> ions occupying all octahedral sites.	NaI, KCl, RbI, RbF
(2) Cesium chloride (CsCl)	$Cs^+ = 8$ $Cl^- = 8$ Both cubic	Not close-packed	CsBr, CsI, TlCl, TlBr, TlI
(3) Zinc blende (ZnS)	$Zn^{2+} = 4$ S <sup>2-</sup> = 4 Both tetrahedral	$S^{2-}$ ions have cubic close-packed arrange- ment with $Zn^{2+}$ ions occupying half of the tetrahedral sites (every alternate site occupied)	CuCI, CuBr, CuI, AgI, BeS
(4) Wurtzite (ZnS)	$Zn^{2+} = 4$ S <sup>2-</sup> = 4 Both tetrahedral	$S^{2-}$ ions have hexa- gonal close-packed arrangement with $Zn^{2+}$ ions occupying half of the tetra- hedral sites.	ZnO, CdS, CdSe, BeO
AB <sub>2</sub> type Crystals			Converting with the
(1) Fluorite (CaF <sub>2</sub> )	$Ca^{2+} = 8$ $F^- = 4$ Cubic and tetrahedral	Ca <sup>2+</sup> ions have cubic closed-packed arrange- ment with $F^-$ ions occupying all the tetrahedral sites.	BaF <sub>2</sub> , SrF <sub>2</sub> , CaF <sub>2</sub> : SrCl <sub>2</sub> , SrCl <sub>2</sub> , BaCl CdF <sub>2</sub> , HgF <sub>2</sub>
(2) Rutile (TiO <sub>2</sub> )	$Ti^{4+} = 6$ $O^{2-} = 3$ Octahedral and triangular	Not close-packed. Ti <sup>4+</sup> ions lie in a sufficiently distorted body- centred cube.	NiF <sub>2</sub> , CoF <sub>2</sub> , FeF <sub>2</sub> , MnF <sub>2</sub> , MgF <sub>2</sub> , ZnF <sub>2</sub> , SnO <sub>2</sub> , PbO <sub>2</sub> , MnO <sub>2</sub> ,

# Table 9.6. Summary of the structure of common ionic crystals

# Calculation of Lattice Energy

Let us calculate the lattice energy of an ionic crystal,  $M^{z+X^{z-}}$  having Na<sup>+</sup>Cl<sup>-</sup> type crystal structure.

At least two forces are operating between the constituent ions of the crystal under consideration. These are :

(i) Electrostatic forces of attraction which arise due to the opposite charges on the ions.

(ii) Repulsive forces which arise due to the overlap of the electron clouds of the ions.

Now let us calculate the magnitude of attractive potential energy and repulsive potential energy of  $M^{z+}X^{z-}$  crystal. The former type of energy is due to the electrostatic forces between the oppositely-charged ions while the latter is due to the repulsive forces arising due to the overlap of the electron clouds of the ions when they are brought nearer to each other from an infinite distance.

Attractive Potential Energy. According to Coulomb's law of inverse square, the electrostatic force of attraction between the oppositely-charged ions varies directly with the product of the charges on the ions and inversely with the square of the distance between them. Thus the force of attraction (F) between the ions  $M^{z+}$  and  $X^{z-}$  of the ionic crystal,  $M^{z+}X^{z-}$  in air is given by :

$$\mathbf{F} = \frac{(z^+ e) (-z^- e)}{r^2}$$

where  $z^+e$  and  $z^-e$  = number of charges of the cation and anion respectively  $z^+$  and  $z^-$  = positive integers (*i.e.*, ionic charge numbers)

e = charge on an electron which is equal to  $4.8 \times 10^{-10} e.s.u$ .

r = inter-ionic distance between the ions.

Now, if one of the ions, under this force of attraction is moved from infinity through a small distance dr, work done in this process will be given by :

Work done

$$=\frac{(z^+e)(-z^-e)}{r^2} dr \qquad ...(A)$$

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The work done in moving one of the ions from infinity through a distance, r will be given by integrating equation (A) between the limits r and  $\infty$  (infinity).

XX7	orl	- 1	on	0
YY	OIL	r u	OII	e

.

$$= \int_{r=\infty}^{r=1} \frac{(z^+e)(-z^-e)}{r^2} dr = \frac{-z^+z^-e^2}{r}$$
$$= \frac{(z^+e)(-z^-e)}{r} \qquad \dots(B)$$

By definition work done given by equation (B) is equal to the electrostatic (or attractive) potential energy between the two ions (*i.e.* potential energy of the ion-pair) viz.  $M^{z+}$  and  $X^{z-}$  separated from each by a distance r.

	Attractive potential energy between M <sup>2+</sup> and	$(z^+e)(-z^-e)$	in
X2-	ions placed at a distance of r from each other	r de la	(C)

Thus, according to Coulomb's law, the potential energy between two ions is equal to the product of their respective charges divided by the distance between the ions [See equation (C)].

Now we know that our ionic crystal contains not only two ions but consists of numberless ions which are arranged in an ordered pattern. Thus in an ionic crystal each ion is surrounded not only by a single ion of opposite charge but also by a number of other ions (positive and negative both). Consequently in order to

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calculate the attractive (electrostatic) potential energy of the crystal we must consider all the interactions given below :

(i) Interaction of a cation with all the anions surrounding it. This interaction gives the *attractive* (*i.e.* electrostatic) *energy*.

(*ii*) Interaction of the same cation with all the cations surrounding it. This interaction gives the *repulsive energy*.

(iii) Interaction of an anion with all the cations surrounding it.

(iv) Interaction of the same anion with all the anions surrounding it.

Considering all the interections mentioned above, we can calculate the potential energy of interaction between different ions of  $M^{z+}X^{z-}$  ionic crystal as follows :

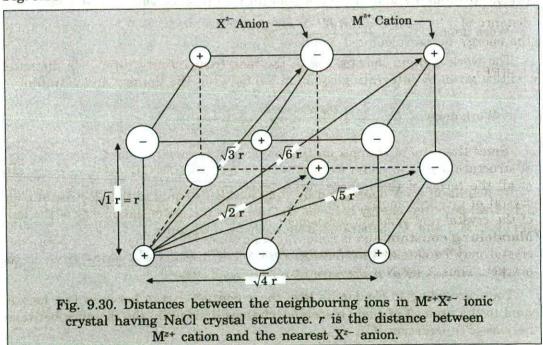
Since, as we have already said, the crystal structure of  $M^{z+}X^{z-}$  crystal is the same as that of NaCl, each  $M^{z+}$  cation is surrounded :

(a) by six  $X^{z-}$  anions at a distance of  $\sqrt{1}r$  or r where r is the distance between  $M^{z+}$  and the nearest  $X^{z-}$ .

(b) by twelve  $M^{z+}$  cations at a distance of  $\sqrt{2r}$ .

(c) by eight  $X^{2-}$  anions at a distance of  $\sqrt{3r}$ .

(d) by six  $M^{z+}$  cations at a distance of  $\sqrt{4}r$  or 2r etc. as is evident from Fig. 9.30



From equation (C) :

(i) The attractive potential energy between  $M^{z+}$  cation and six  $X^{z-}$  anions which are placed at a distance of  $\sqrt{1}r$  from  $M^{z+}$  cation.

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$$=\frac{(z^+e)\times 6(-z^-e)}{\sqrt{1}r}=\frac{-6\,z^+z^-e^2}{\sqrt{1}r}$$

(*ii*) The repulsive potential energy between  $M^{z+}$  cation and twelve  $M^{z+}$  cations which are placed at a distance of  $\sqrt{2}r$  from  $M^{z+}$  cation.

$$=\frac{(z^+e)\times 12\,(z^+e)}{\sqrt{2}r}=\frac{12\,(z^+)^2\,e^2}{\sqrt{2}r}$$

(*iii*) The attractive potential energy between  $M^{z+}$  cation and eight  $X^{z-}$  anions which are placed at a distance of  $\sqrt{3}r$  from  $M^{z+}$  cation

$$=\frac{(z^+e)\times 8(-z^-e)}{\sqrt{3}r}=\frac{-8z^+z^-e^2}{\sqrt{3}r}$$

(*iv*) The repulsive potential energy between  $M^{z+}$  and six  $M^{z+}$  cations which are placed at a distance of  $\sqrt{4r}$  from  $M^{z+}$  cation.

$$=\frac{(z^+e)\times 6(z^+e)}{\sqrt{4}r}=\frac{6(z^+)^2e^2}{\sqrt{4}r}$$

Thus the value of attractive (or electrostatic) potential energy of  $M^{z+}$  cation,  $(PE)_{M^{z+}}$  when we consider the interaction of this cation with all other ions (cations and anions both) surrounding it like six  $X^{z-}$  anions placed at a distance of  $\sqrt{1}r$ , twelve  $M^{z+}$  cations placed at a distance of  $\sqrt{2}r$ , eight  $X^{z-}$  anions placed at a distance of  $\sqrt{3}r$  and so on in  $M^{z+}X^{z-}$  ionic crystal is obtained by summing up all the energy terms calculated as above. Thus :

$$(\text{PE})_{\text{M}^{s+}} = \frac{-6}{\sqrt{1}r} \frac{z^{*}z^{-}e^{2}}{\sqrt{2}r} + \frac{12(z^{*})^{2}e^{2}}{\sqrt{2}r} - \frac{8z^{*}z^{-}e^{2}}{\sqrt{3}r} + \frac{6(z^{*})^{2}e^{2}}{\sqrt{4}r} + \dots$$
$$= -\frac{z^{*}z^{-}e^{2}}{r} \left(\frac{6}{\sqrt{1}} - \frac{12z^{*}}{\sqrt{2}z^{-}} + \frac{8}{\sqrt{3}} - \frac{6z^{*}}{\sqrt{4}z^{-}} + \dots\right) \dots (z)$$

Since the ratio of charges on the ions  $(z^+/z^-)$  is constant for a particular type of structure (e.g.  $z^+/z^-$  ratio for NaCl = 1,  $z^+/z^-$  ratio for CaF<sub>2</sub> = 2 etc). the sum of all the terms of the infinite series given in bracket is constant for an ionic crystal of given geometry. The value of this constant depends on the geometry of the crystal and remains indepedent of the value of r. This constant is called **Mandelung constant** and is generally represented by A. The value of A for NaCl crystal may be obtained by putting  $z^+/z^- = 1$  in the infinite series given in the bracket. Thus A for NaCl is given by :

$$A_{\text{NaCl}} = \left(\frac{6}{\sqrt{1}} - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{\sqrt{4}} + \dots\right)$$
  
= 1.7476.

As a matter of fact the value 1.7476 is the value of the Mandelung constant for all those ionic crystals which have NaCl type structure. Values of Mandelung constants for other ionic crystals can be derived by a similar method. These values for some ionic crystals are given below in Table 9.7.

Crystal structure	Values of Mandelung constant (A)
Sodium chloride (NaCl)	1.7476
Caesium chloride (CsCl)	1.7627
Zinc blende or sphalerite (ZnS)	1.6381
Wurtzite (ZnS)	1.6413
Fluorite (CaF <sub>2</sub> )	2.5193
Rutile (TiO <sub>2</sub> )	2.4080
Corundum (Al <sub>2</sub> O <sub>3</sub> )	4.1718
Anastase (TiO <sub>2</sub> )	4.800
Cadmium iodide (CdI <sub>2</sub> )	4.71
$\beta$ -quartz (SiO <sub>2</sub> )	4.4394

Table 9.7. Values of Mandelung constant (A values) for different crystal structure.

Thus writting A (Mendelung constant) for the sum of all the terms of the infinite series given in bracket in equation (i) we get :

$$(PE)_{M^{2+}} = -\frac{z^{+}z^{-}e^{2} A}{r} \qquad \dots (ii)$$

Now when we consider the interaction of  $X^{z-}$  anion with all other ions (cations and anions both) surrounding it, the value of electrostatic potential energy of this anion,  $(PE)_X^{z-}$  can be calculated by using the same procedure as employed for the calculation of  $(PE)_M^{z+}$ . The value of  $(PE)_M^{z-}$  comes out to be the same as that of  $(PE)_M^{z+}$  given by equation ( $\ddot{u}$ ), since cations and anions have the same arrangement of ions surrounding them in NaCl structure. Thus :

$$(\text{PE})_{X^{z-}} = (\text{PE})_{M^{z+}} = -\frac{z^+ z^- e^2 A}{r}$$
 ...(*iii*)

The total attractive or electrostatic interaction potential energy.  $(PE)_{attraction}$  is then given by half the sum of  $(PE)_{M}^{z+}$  and  $(PE)_{X}^{z-}$ , *i.e.* 

$$(PE)_{attraction} = \frac{1}{2} [(PE)_{M^{2+}} + (PE)_{X^{2-}}]$$
  
=  $\frac{1}{2} \left[ -\frac{z^{+}z^{-}e^{2}}{r} - \frac{z^{+}z^{-}e^{2}}{r} \right]$   
=  $-\frac{z^{+}z^{-}e^{2}}{r} - \frac{z^{+}z^{-}e^{2}}{r} - \frac{z^{+}z^{-}e^{2}}$ 

The factor  $\frac{1}{2}$  is needed since the addition of  $(PE)_M^{z+}$  and  $(PE)_X^{z-}$  takes the interaction in account twice.

**Repulsive Potential Energy.** So far we have considered only the attraction between the ions but when the ions are brought near to each other from an infinite distance, they also repell each other due to the overlap of their electron clouds. Thus the attraction between the ions is also opposed by the repulsion between them. In other words, the total attractive interaction potential energy,  $(PE)_{attraction}$  which represents a net attraction between ions, is opposed by repulsive

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potential energy,  $(PE)_{repulsion}$ . A number of expressions have been suggested for the repulsive potential energy. According to one expression given by Born and Lande,  $(PE)_{repulsion}$  is inversely proportional to the *nth* power of the distance, *r* between the ions. Thus according to them,  $(PE)_{repulsion}$ , is given by the expression :

$$(PE)_{repulsion} = \frac{B}{r^n} \qquad \dots (v)$$

Here B is a constant which is called **Born coefficient** or **repulsion coefficient** and is approximately proportional to the number of nearest neighbours (*i.e.* coordination number). This constant expresses the repulsion between the ions. nis another constant which is called **Born exponent** and can be estimated by compressibility measurements. Average value of Born exponent (n values) for different electronic configurations of the ions are given in Table 9.8.

# Table 9.8. Average values of Born exponent (*n*-values) for different electronic configurations of ions.

Electronic configuration	n values	Examples
He	5	Li <sup>+</sup> , Be <sup>2+</sup>
Ne	7	Na <sup>+</sup> , Mg <sup>2+</sup> , O <sup>2-</sup> , F <sup>-</sup>
Ar	9-0006	K <sup>+</sup> , Ca <sup>2+</sup> , S <sup>2-</sup> , Cl <sup>-</sup> , Cu <sup>+</sup>
Kr	10	Rb <sup>+</sup> , Br <sup>-</sup> , Ag <sup>+</sup>
Xe	12	Cs <sup>+</sup> , I <sup>-</sup> , Au <sup>+</sup>
Rn	14	

*n*-values of an ionic crystal composed of ions having different configurations (*i.e.* non-isoeleotronic ions) is taken as an average of the *n*-values of the two constituent ions, *e.g. n*-value of NaCl in which Na<sup>+</sup> and Cl<sup>-</sup> ions are not isoelectronic is given by :

*n*-value of 
$$NaCl = \frac{1}{2}(n\text{-value of } Na^+ + n\text{-value of } Cl^-)$$
  
=  $\frac{1}{2}(7+9) = 8$ 

Thus the total potential energy,  $(PE)_{total}$  of a pair of ions separated by a distance of r within the ionic crystal,  $M^{z+}X^{z-}$  which has NaCl type structure and for which all the types of forces due to the neighbouring ions have been considered, is given by the sum of  $(PE)_{attraction}$  and  $(PE)_{repulsion}$ . Thus :

$$(PE)_{total} = (PE)_{attraction} + (PE)_{repulsion}$$
$$= \left[ -\frac{z^{*}z^{-}e^{2} A}{r} + \frac{B}{r^{n}} \right] \text{ per ion-pair } \dots(vi)$$

The energy given by equation (vi) is the energy released when  $M^{z+}X^{z-}$  crystal is formed at a distance of r between  $M^{z+}$  cation and  $X^{z-}$  anion. In other words  $(PE)_{total}$  is the energy released when a cation  $(M^{z+})$  and an anion  $(X^{z-})$  separated by an infinite distance are brought nearer to each other until they are separated by a distance r.  $(PE)_{total}$  is the potential energy of an ion-pair separated by a distance r. **Estimation of the value of B.** The value of B can be estimated by utilising the fact that at equilibrium distance between the ions in the crystal  $(r_0)$ , the attractive and repulsive forces in the crystal are exactly balanced and hence the value of  $(PE)_{total}$  becomes minimum, *i.e.* when  $r = r_0$ , d (PE)/dr = 0. Thus :

$$\left(\frac{d \text{ (PE)}}{dr}\right)_{r=r_0} = \frac{d}{dr} \left(-\frac{z^+ z^- e^2 \mathbf{A}}{r} + \frac{\mathbf{B}}{r^n}\right) = 0$$
$$= \frac{z^+ z^- e^2 \mathbf{A}}{r_0^2} - \frac{n\mathbf{B}}{r_0^{n+1}} = 0$$
$$\frac{z^+ z^- e^2 \mathbf{A}}{r_0^2} = \frac{n\mathbf{B}}{r_0^{n+1}}$$
$$\mathbf{B} = \frac{z^+ z^- e^2 \mathbf{A} r_0^{n-1}}{n}$$

Now put the above value of B and  $r = r_0$  in equation (vi) to get :

$$(PE)_{r=r_0} = \frac{z^+ z^- e^2 A}{r_0} + \frac{z^+ z^- e^2 A r_0^{n-1}}{n r_0^n}$$
  
=  $-\frac{z^+ z^- e^2 A}{r_0} \left(1 - \frac{1}{n}\right)$  per ion-pair in cgs units ....(vii)

Potential energy,  $(PE)_{r=r_0}$  given by equation (vii) is the energy released when a gaseous cation  $(M^{z+})$  and a gaseous anion  $(X^{z-})$  separated from each other by an infinite distance are brought to an equilibrium distance  $(r_0)$  to form the ionic crystal,  $M^{z+}X^{z-}$ . Consequently potential energy released, when N gaseous cations and N gaseous anions (N is the Avogadro's number which is defined as the number of molecules in a gram molecule and has the value  $6.0238 \times 10^{23}$  atoms/ g. atom) separated from each other by an infinite distance are brought to their equilibrium distance  $(r_0)$  to form a mole of the ionic crystal, is obtained by multiplying  $(PE)_{r=r_0}$  by N. The product,  $(PE)_{r=r_0} \times N$ , by definition, gives the lattice energy (U) of the crystal, *i.e.*,

 $(\text{PE})_{r=r_0} \times \text{N} = \text{Lattice energy (U)}$ 

$$= -\frac{z^{+}z^{-}e^{2} \text{ AN}}{r_{0}} \left(1 - \frac{1}{n}\right) \text{ per mole (in cgs units)} \qquad \dots(viii)$$
$$U = -\frac{z^{+}z^{-}e^{2} \text{ AN}}{r_{0}} \left(1 - \frac{1}{n}\right) \text{ per mole} \qquad \dots(ix)$$

or

Equation (*ix*) gives the potential energy of one mole of the crystal and is called **Born-Lande equation.** The derivation of the above equation is based on the assumption that both the cations and anions are hard spheres and the solid has an essentially ionic structure, *i.e.* the ions are *not distorted* (*i.e. polarised*) by the neighbouring ions. If the ions are distorted, M—X bonds achieve some covalent character and hence the lattice energy calculated from Born-Lande

or

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equation differs considerably form that found experimentally (e.g. by Born-Haber cycle) as is evident from Table 9.9. Consequently the difference in the calculated and experimental values of lattice energy of an ionic solid is due to some covalent character in the solid. This covalent character is developed due to the polarisation of ions.

AlkaliCalculated values frommetalBorn-Lende equationhalides[Equ. (ix)]		Experimental values from Born-Haber cycle
LiF	240.8	247.2
LiCl	193.9	200.8
LiBr	183.1	186.7
LiI	169.3	171.7
NaF	215.6	218.5
NaCl	182.0	184.0
NaBr	171.8	174.1
NaI	158.5	162.7
KF	190.6	194.1
KCl	164.3	167.6
KBr	157.6	160.4
KI	148.9	151.1
RbF	181.9	186.5
RbCl	158.9	163.1
RbBr	152.1	156.3
RbI	144.0	147.4
CsF	172.8	177.8
CsCl	148.8	150.5
CsBr	143.3	146.4
CsI	135.8	139.7

### Table 9.9. Calculated and experimental values of lattice energies of alkali metal halides (Kcal/mole)

Theoretical values calculated by Born-Lande equation can be improved by taking into account the following :

(i) Van der Waals forces between the ions

(ii) Zero point vibrational energy of the ions

(iii) Resonance energy which arises because all ionic bonds have some covalent character.

**Example.** Calculate the lattice energy of NaCl crystal with the help of Born-Lande equation.

**Solution.** The Born-Lande equation can be used as follows for the calculation of lattice energy of NaCl crystal by using the following values of various constant  $z^+ = z^- = 1$ ;  $e = 4.8 \times 10^{-10} esu$ ; A = 1.7476;  $N = 6.0238 \times 10^{23}$  atoms/g. atom;  $r_0 = (r_{\text{Na+}} + r_{\text{CI}})A^\circ = (0.95 + 1.81)$  Å = 2.76 $A^\circ = 2.76 \times 10^8$  cm;  $n = \frac{1}{2}(7 + 9) = 8$ 

Now,  $U = -\frac{z^{+}z^{-}e^{2}AN}{r_{0}} \left(1 - \frac{1}{n}\right)$   $\therefore \qquad U_{\text{NaCl}} = -\frac{1 \times 1 \times (4.8 \times 10^{-10} \ esu)^{2} \times 1.7476 \times 6.0238 \times 10^{23}}{2.76 \times 10^{8} \ cm} \left(1 - \frac{1}{8}\right)$   $= -7.70 \times 10^{12} \ \text{ergs/mole} \qquad \left[\because \frac{(esu)^{2}}{cm} = \text{erg.}\right]$  $= -184.03 \ \text{Kcal/mole} \qquad \left[\because 1 \ \text{erg} = 2.390 \times 10^{-11} \ \text{Kcall.}\right]$ 

This value agrees closely with the experimentally determined value of 180 Kcal/mole.

It may be seen from Table 9.9 that the calculated and experimetal values agree to some extent. But in case of salts which contain ions of high charge or pseudo-intert gas type cations, the experimental values are much higher than the calculated values and hence the agreement between calculated and experimental values is very poor as is evident from the values of some salts given below :

Salt	Calculated value of lattice energy (kcal/mole)	Experimental value of lattice energy (kcal/mole)
$MnI_2$	481	563
$FeI_2$	493	589
CoI2	502	605
PbI <sub>2</sub>	460	510
$Ag_2O$	585	714
CuS	612	673
HgS	774	854

The discrepencies between the calculated and experimental values are due to the fact that these salts, although predominantly ionic, also contain substantial amount of covalent character.

**Experimental Determination of Lattice Energy by Born-Haber Cycle.** The lattice energy of an ionic solid can be determined experimentally by a process known as **Born-Haber cycle** devised by Born-Haber in 1919. Let us illustrate this cycle by considering NaCl ionic crystal. The determination of lattice energy of NaCl by this cycle is based on the assumption that the formation of one mole of crystalline NaCl can occur by any of the following two processes.

1. Process consisting of direct combination of Na(s) and  $\frac{1}{2}$  Cl(g) to form NaCl(s). In this process one gram atom of sodium, Na(s) and half mole of chlorine gas,  $\frac{1}{2}$  Cl<sub>2</sub>(g) are combined together to form one mole of crystalline sodium chloride, NaCl(s). In this reaction heat, called *heat of formation* of NaCl(s) (represented

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by Q) is also produced. Thus it is an exothermic reaction. Heat produced is shown with a negative sign. Thus :

$$Na(s) + \frac{1}{2}Cl_2(g) \rightarrow NaCl(s); Heat produced = Heat of formation of NaCl(s) = -Q$$

2. Process consisting of the following five steps (a) Conversion of Na atoms from solid state to gaseous state  $[Na(s) \rightarrow Na(g)]$ . Here solid sodium, Na(s) is converted into gaseous state, Na(g). This type of conversion is called sublimation. In this reaction heat, called heat of sublimation of sodium (represented by S) is required, *i.e.* it is an endothermic reaction. Heat required (or absorbed) in a reaction is shown with a positive sign. Thus :

 $Na(s) \rightarrow Na(g)$ ; Heat required = Heat of sublimation of Na = + S

(b) Conversion of Na(g) into  $Na^{+}(g)$  ion  $[Na(g) \rightarrow Na^{+}(g) + e^{-}]$ . Here sodium atom in the gaseous state, Na(g) formed in step (a) gives up an electron and is converted into gaseous ion,  $Na^{+}(g)$ . This type of conversion is called *ionisation*. For this reaction, energy, called ionisation energy of sodium atom (represented as I) is required, *i.e.* this reaction is an *endothermic reaction*. Thus :

 $Na(g) \rightarrow Na^+(g) + e^-$ ; Energy required = Ionisation energy of Na atom = + I

(c) Conversion of  $\frac{1}{2}Cl_2(g)$  molecule into Cl(g) atom  $[\frac{1}{2}Cl_2(g) \rightarrow Cl(g)]$ . Here chlorine molecule in the gaseous state,  $Cl_2(g)$  is converted into gaseous chlorine atom, Cl(g). This type of conversion is called *dissociation*. For this reaction heat, called *heat of dissociation of chlorine molecule* (represented as D) is required, *i.e.* this conversion is an *endothermic reaction*. Thus :

 $\frac{1}{2}$ Cl<sub>2</sub>(g)  $\rightarrow$  Cl(g); Heat required =  $\frac{1}{2} \times$  Heat of dissociation of Cl<sub>2</sub>(g) molecule

 $= + \frac{1}{2}D$ 

(d) Conversion of Cl(g) into  $Cl^{-}(g)$  [ $Cl(g) + e^{-} \rightarrow Cl^{-}(g)$ ]. Here chlorine atom in the gaseous state,  $Cl^{-}(g)$  formed in step (c) adds up an electron given up by Na(g) in step (b) and is converted into gaseous ion,  $Cl^{-}(g)$ . In this reaction energy, called *electron affinity energy* of Cl atom (represented as E) is *produced*, *i.e.* this conversion is an *exothermic reaction*. Thus :

 $Cl(g) + e^{-}[Lost by Na(g) in step (b)] \rightarrow Cl^{-}(g); Heat produced$ 

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= Electron affinity of Cl atom

= -E

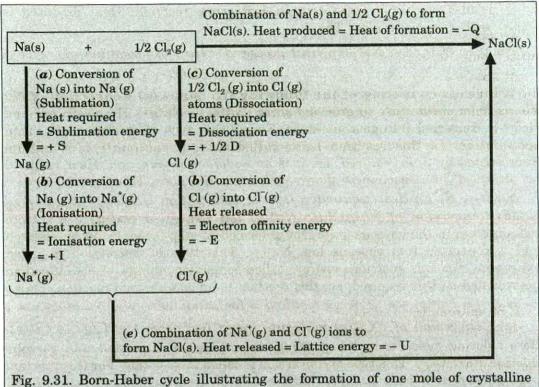
(e) Combination of Na<sup>+</sup>(g) and Cl<sup>-</sup>(g) ions to form NaCl(s) [Na<sup>+</sup>(g) + Cl<sup>-</sup>(g)  $\rightarrow$  NaCl(s)]. Na<sup>+</sup>(g) and Cl<sup>-</sup>(g) ions formed in steps (b) and (d) respectively combine together and form one mole of solid sodium chloride, NaCl(s). Here attractive forces between Na<sup>+</sup>(g) and Cl<sup>-</sup>(g) operate and hence energy of the system is decreased, *i.e.* this reaction is accompanied by the release of energy (exothermic reaction) which is obviously called *lattice energy* (U) of NaCl(s). Thus :

 $Na^+(g) + Cl^-(g) \rightarrow NaCl(s); Energy \ released = Lattice \ energy \ of \ NaCl(s) = -U$ 

Diagramatically the formation of one mole of crystalline sodium chloride NaCl(s) by the two processes mentioned above has been shown in Fig. 9.31 which is called **Born-Haber cycle**.

...(1)

(Delhi B.Sc. Hons. 1972)



sodium chlorine, NaCl(s). Positive sign associated with energy symbols indicates the absorption of energy (energy required) while the negative sign indicates the release of energy (energy released or produced).

Since the two processes are independent of each other, by Hess's law the heat of formation of NaCl(s), Q must be equal to the sum of all other energy terms. Thus :

$$-\mathbf{Q} = +\mathbf{S} + \mathbf{I} + \frac{1}{2}\mathbf{D} - \mathbf{E} - \mathbf{U}$$

With the help of this equation we determine the value of U, if the quantitative values of other energy terms are known. The quantitative value of each term is substituted in the above equation along with its sign.

Solved Example. When a mole of crystalline NaCl is prepared from 1 gram atom of Na and 0.5 mole of chlorine gas, 410 KJ of heat is produced. The heat of subilmation of Na metal 108.8 KJ. The heat of dissociation of chlorine gas into atoms is 242.7 KJ, the ionisation energy of Na is 493.7 KJ and the electron affinity of Cl is 368.2 KJ. Calculate the lattice energy of NaCl.

Solution. Here Q = 410 KJ, S = 108.8 KJ, I = 493.7 KJ, D = 242.7 KJ, E = 368.2 KJ and U is to be calculated. Substituting these values, along with their signs, in equation (1) given above, we get :

or 
$$-410 = 108.8 + 493.7 + \frac{1}{2} \times 242.7 \times 368.2 + U$$
  
or  $-410 = 355.65 + U$   
or  $U = -410 - 355.65 = -765.65$  KJ/mole.

### **Defects in Crystals**

An ideal crystal is that which has the same unit cell containing the same lattice points throughout the whole crystal.

At absolute zero most of the ionic crystals contain well-ordered arrangement of constituent ions and hence the crystals have no imperfections or defects. With the rise of temperature, one or more the lattice sites become unoccupied or vacant and this gives rise to a defect in the regular arrangement of the constituent ions of the crystal. The number (n) of such defects per cm<sup>3</sup> at a given temperature (T) is given by :

$$n = N.e^{-w/2RT}$$

Here  $N = \text{total number of sites per cm}^3$ ; w = work (energy) required to produce a defect; R = gas constant and e = base of natural logrithm.

Above discussion makes it evident that above absolute zero all crystalline solids have defects in the regular arrangement of the constituent ions of which the ionic crystals are composed. These defects are of two types : (1) Stoichiometric defects, and (2) Non-stoichiometric defects.

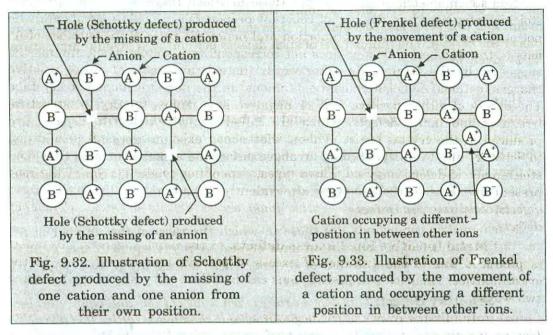
### **1. Stoichiometric Defects**

Stoichiometric compounds are those in which the ratio of the number of  $A^+$  ions to the number of  $B^-$  ions (in an ionic crystal,  $A^+B^-$ ) is equal to one, *i.e.* the number of  $A^+$  ions is equal to that of  $B^-$  ions. These defects are of two types : (i) Schottky defect, and (ii) Frankel defect.

(i) Schottky Defect. This defect arises when some cations and equal number of anions are missing from their own position and thus leave lattice vacancies or holes in the crystal lattice. Thus some holes are created due to the missing of cations and equal number of holes are created due to the missing of anions. This defect created due to the missing of one cation and one anion is illustrated in Fig. 9.32. Since the number of missing cations is equal to the number of missing anions, the crystal as a whole remains neutral. In this defect the missing cations and missing anions leave their original position and move to the surface. This defect is mostly found in compounds (i) which have high coordination numbers (ii) in which the ions (both cations and anions) are almost of the same size, i.e. the radius ratio.  $r_{+}/r_{-}$  is not far below unity. Thus alkali metal halides like NaCl (C.N. = 6) and CsCl (C.N. = 8) have Schottky defect.

(ii) **Frenkel Defect.** This defect arises when one of the ions (mostly cation) leaves its own position and occupies another one (hole) in between other ions in the lattice. Cations, being smaller in size, are more likely than the anions to leave their own position and occupy the other one in between the ions in the lattice. It may be noted that here again, since the number of cations is equal to that of anions, the crystal as a whole remains neutral. In this defect the cation moves to another position between the two layers and is thus surrounded by a greater number of anions. (See Fig. 9.33). This defect is mostly found in compounds (i) which have low coordination number (ii) in which the negative ions are much larger in size than the positive ions, i.e. the radius ratio  $r_+/r_-$  is low, and

(iii) which have a highly polarising cation and an easily polarisable anion. ZnS (both zinc blonde and wurtzite), AgBr etc. are the examples of compounds having Frenkel defect. In ZnS, some of the  $Zn^{2+}$  ions are missing from their regular positions and occupy positions in between other ions. Similarly in AgBr, some of Ag<sup>+</sup> ions are entrapped in the interstitial space and thus holes are created in the lattice.



Solids generally contain both the types of defects mentioned above, but one is more prominent than the other. The number of defects in a crystal increases generally with the increase of temperature. For example at room temperature NaCl ionic crystal has one defect for  $10^{15}$  lattice sites while at 500°C it has  $10^9$ defects for the same number of lattice sites. Normally, Schottky defects are easier to form than Frenkel defects, since the former require less energy for their formation.

**Consequences of Schottky and Frenkel Defects.** (a) We have seen that in Frenkel defect similar charges come closer to each other. This closeness leads to an increase in the dielectric constant of the crystal.

(b) We have seen that is Schottky defect, the number of ions in the lattice of the crystal is decreased and this decrease in the number of ions decreases the density of the ionic solids.

(c) The presence of holes in both types of defects lowers the lattice energy or stability of the crystal.

(d) As a result of both the types of defects, the crystal is able to conduct electric current when electric field is applied between the two ends of a crystal. The conduction of electric current takes place by an ionic mechanism. In this mechanism, when an electric field is applied, a near-by ion leaves its original

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position and occupies another one (hole). This results in creating a new hole and another near-by ion leaves its original position and occupies this new hole and so on. This process continues and a hole migrates from one end to the other end and the conduction of electric current takes place in the whole crystal.

### 2. Non-stoichiometric Defects

Non-stoichiometric compounds are those in which there is a departure from stoichiometry based on the law of constant proportions, *i.e.* these compounds do not obey the law of constant proportion and hence the ratio of the number of  $A^+$  ions to the number of  $B^-$  ions does not correspond to a simple whole number as suggested by the formula. In other words there is an excess of either positive charges (cations) or negative charges (anions) in the non-stoichiometric crystals. The excess of either positive ions or negative ions makes the crystal structure irregular and hence defects, which are called *non-stoichiometric defects*, are produced in the crystal lattice. These defects may exist in a crystal in addition to Schottky and Frenkel defects. The above discussion makes it evident that non-stoichiometric defects may be of two types, depending on the nature of the ions present in excess. These two types are evidently : (*i*) Metal (positive ions) excess defects, and (*ii*) Non-metal (negative ions) excess defects or metal deficiency defects.

(i) Metal (positive ions) excess defects. As the name suggests, this defect is produced due to the presence of excess of positive ions (metal) ions in the crystal lattice. The excess of positive ions can be achieved by any of the following two ways :

(a) In the first way, one of the negative ions is missing from its real position, leaving a hole and this hole is occupied by an extra free electron so that the neutral nature of the crystal lattice may be maintained (Fig. 9.34). The negative ion leaves the surface in the form of gas. For example, when excess of Na is burnt in  $Cl_2$ , we get yellow NaCl. The yellow colour is produced because the Clions leave the lattice and electrons occupy their position.

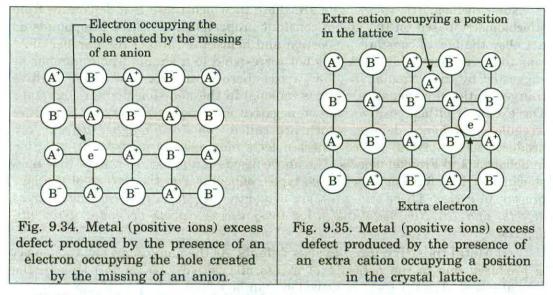
> Na<sup>+</sup> Cl<sup>-</sup> Na<sup>+</sup> Cl<sup>-</sup> Cl<sup>-</sup> Na<sup>+</sup>  $e^-$  Na<sup>+</sup> Na<sup>+</sup> Cl<sup>-</sup> Na<sup>+</sup> Cl<sup>-</sup>

The electrons occupying the position vacated by the missing anions (Cl<sup>-</sup> ions) are called *F* centres. (F = Farbe which is a German word and means colour). This defect is found in those crystals which have Schottky defects. Note that this defect contains only one hole which is occupied by an extra electron while the Schottky defect has two holes.

(b) In the second way, an extra positive ion occupies a position in the lattice and in order to maintain the electrical neutrality of the crystal an electron also occupies a position in the lattice (Fig. 9.35). This defect is found in those crystals which have Frenkel defects. This defect has no hole while Frenkel defect contains one hole in the lattice.

**Consequences of Metal Excess Defects** (a) The crystals having metal excess defects produced by any of the above two ways contain *free electrons*. Such

crystals can, therefore, conduct electricity to some extent with the help of these free electrons. Since the number of free electrons in such crystals is very small, such crystals can conduct small amount of electricity. The amount of electricity conducted by such crystals is smaller even than that conducted by metals, fused salts and water solution of salts. It is for this reason that the crystals having metal excess defects are called **semiconductors**.



(b) Due to the presence of free electrons, the crystals having metal excess defects are generally coloured. The free electrons get excited easily to higher energy levels by the absorption of certain wavelength from the visible white light and, therefore, the compounds appear coloured. For example non-stoichiometric sodium chloride is *yellow* and zinc oxide which is white in cold, *appears yellow when hot*.

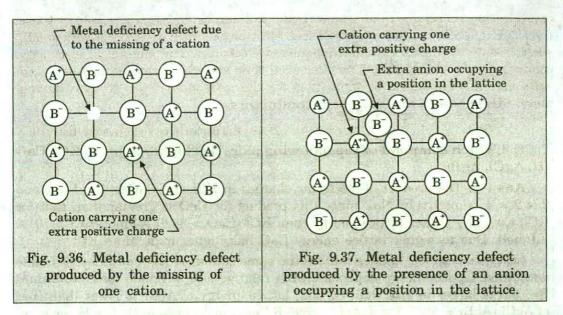
(*ii*) Non-metal (negative ions) excess defects or metal deficiency defects. As the name suggests, this defect is produced by the presence of excess of negative ions in the crystal lattice. The excess of negative ions can be achieved by any of the following ways :

(a) In the first way, one of the positive ions is missing from its position and in order to keep the electrical neutrality of the crystal, one of the adjascent cations acquires one extra positive charge on it, becoming  $A^{2+}$  (Fig. 9.36). The cation  $A^+$  acquiring are extra positive charge on it should be able to exhibit variable valency, *i.e.* such a cation should be of transition metals.

(b) In the second way, an extra negative ion occupies a position in the lattice and in order to maintain the electrical neutrality of the crystal, one of the adjascent cations acquires an extra positive charge on its becoming  $A^{2+}$  (Fig. 9.37).

Here it is essential to understand that since the size of the anions is usually large, it is difficult for the anions to fit into the interstitial sites. As a matter of fact, no crystals containing extra anions occupying the interstitial positions in the crystal lattice are known and hence the metal deficiency defect shown in Fig. 9.37 represents only a *theoretical prediction or possibility*.

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**Consequences of Metal Deficiency Defects.** We have seen that in metal deficiency defects one of the cation, say  $A^+$ , is changed into  $A^{2+}$  cation. This type of conversion takes place through the movement of an electron from  $A^+$  to  $A^{2+}$ . Such type of movement is called *movement of positive hole* and makes the crystals showing metal deficiency defects behave as semi-conductors. Consequently the crystals which contain metal deficiency defects also act as semi-conductors.

## **Questions with Answers**

Q.1 Which of the following alkali metal halides has the lowest lattice energy.

(a) LiF (b) NaCl (c) KBr (d) CsI.

Ans : (d).

**Explanation.** We know that lattice energy of an ionic salt decreases with the increase of the size of its cation and with the increase of the size of its anion. Thus an ionic salt having the largest cation and largest anion has the lowest lattice energy. Thus since  $Cs^+$  ion is the largest cation among  $Li^+$ ,  $Na^+$  and  $K^+$  ions and  $I^-$  ion is the largest anion among  $F^-$ ,  $Cl^-$  and  $Br^-$  ions, CsI has the lowest value for its lattice energy.

Q.2 CaO and NaCl have same crystal structure and approximately the same inter-ionic distance. Calculate the ratio between  $U_{CaO}$  and  $U_{NaCl}$ .

Ans : We know that :

Lattice energy of an ionic crystal =  $\frac{q_1 \times q_2}{r^2}$ ,

where  $q_1$  and  $q_2$  are the charges on cation and anion and r is the inter-ionic distance. Since r is the same for NaCl and CaO,

$$U_{\text{NaCl}} = \frac{(+1) \times (-1)}{r^2} = \frac{-1}{r^2}$$
$$U_{\text{CaO}} = \frac{(+2) \times (-2)}{r^2} = \frac{-4}{r^2}$$
$$\therefore \frac{U_{\text{CaO}}}{U_{\text{NaCl}}} = \frac{-4}{r^2} \times \frac{r^2}{-1} = 4 \text{ (Ans.)}$$

Q.3 Which compond of the following pairs has higher *m.pt.* (i) KCl, CaO (ii) AgCl, AgBr.

Ans: (i) The product of electronic charges in KCl and CaO is  $1 \times 1 = 1$  and  $2 \times 2 = 4$  respectively. Now since this product for CaO is greater than that for KCl, CaO has higher lattice energy than KCl (CaO = 3520 KJ/mol, KCl = 701.2 KJ/mol). Due to higher lattice energy CaO has higher m.pt. than KCl.

(*ii*) Since both the halides contain the same cation  $viz \operatorname{Ag}^+$  but different halide ions, their lattice energy depends on the relative size of halide ions. Now since Br<sup>-</sup> ion is larger in size than Cl<sup>-</sup> ion, lattice energy of AgBr is lower than that of AgCl (AgBr = 883KJ/mol, AgCl = 895 KJ/mol) and hence AgBr has lower m.pt. than AgCl (AgBr = 434°C, AgCl = 455°C), *i.e.* AgCl has higher m.pt. than AgBr.

Q.4 Which of the following species has the highest lattice energy ? LiF, LiCl, NaCl and MgO.

**Ans :** The given species can be represented as  $Li^+F^-$ ,  $Li^+ Cl^-$ ,  $Na^+Cl^-$  and  $Mg^{2+} O^{2-}$ . We know that lattice energy increases with the increase of charges on the ions. Now since MgO has +2 charges on Mg and -2 charges on O-atom, it has the highest lattice energy.

Q.5 If the close packed cations in an AB type solid have a radius of 75 pm, what would be the maximum and minimum sizes of the anions filling the voids ?

**Ans**: Since the cations in AB solid have cubic (fcc) unit cell or NaCl type structure and hence C.N. of each ion = 6. Thus the value of  $r_{A^+}/r_{B^-}$  should lie in the range 0.414 - 0.732, *i.e.* 

$$\frac{r_{A^+}}{r_{B^-}} = 0.414 - 0.732$$

or

$$\frac{1}{r_{\rm c}} = 0.414 - 0.732$$

(a) Maximum value of  $r_{B^-}$ ,  $(r_{B^-})_{max}$  is obtained, if

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$$\frac{75}{(r_{\rm B^-})_{\rm max}} = 0.414$$

or

$$(r_{\rm B^-})_{\rm max} = \frac{75}{0.414} \text{ pm} = 181.2 \text{ pm}$$
 (Ans.)

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(b) Minimum value of  $r_{B^-}$ ,  $(r_{B^-})_{mini}$  is obtained, if

$$\frac{75}{(r_{\rm B^-})_{\rm mini}} = 0.732$$

or

...

$$(r_{\rm B^-})_{\rm mini} = \frac{75}{0.732} \, \rm pm = 102.5 \, \rm pm$$
 (Ans.)

Q.6 (i) Br<sup>-</sup> ions form a close packed structure. If the radius of Br<sup>-</sup> ion is 195 pm, calculate the radius of the cation that just fits into the tetrahedral hole.

(ii) Can a cation A<sup>+</sup> having a radius of 82 pm be slipped into the octahedral hole of the crystal A<sup>+</sup> Br<sup>-</sup>?

Ans: (i) Radius of the cation that can just fit into the tetrahedral hole should be equal to the radius of tetrahedral hole. Thus :

Radius of cation = Radius of tetrahedral void (hole)

= 0.225 × Radius of Br<sup>-</sup> ions having close-packed structure  $= 0.225 \times 195 \text{ pm} = 43.87 \text{ pm}$  (Ans)

(*ii*) Radius ratio 
$$=\frac{r_{A^+}}{r_{B^-}} = \frac{82}{195} = 0.4205$$

Since the value of  $r_{A^+}/r_{Br^-}$  lies in the range 0.414 - 0.732, cation A<sup>+</sup> can fit into the octahedral hole.

Q.7 In a mixed oxide, oxide ions have ccp arrangement. Cations A occupy 12.5% of tetrahedral holes and cations B are present in 50% of octahedral holes. What is the simplest formula of the mixed oxide?

**Ans**: Since oxide ions  $(O^{2-})$  have *ccp* arrangement, each  $O^{2-}$  ion has two tetrahedral holes and one octrahedral hole.

12.5% of two tetrahedral holes =  $\frac{2 \times 12.5}{100} = 0.25 = \frac{1}{4}$ China interferences interior 50% of one octahedral hole  $=\frac{1\times50}{100}=\frac{1}{2}$ 

No. of A cations per  $O^{2-}$  ion =  $A_{1/4}$ 

No. of B cations per  $O^{2-} = B_{1/2}$ 

Formula of the mixed oxide =  $A_{1/4} B_{1/2} O = AB_2O_4$  (Ans) 1

Q.8 If AgI crystallises in a zinc blend structure with I<sup>-</sup> ions forming the lattice, then calculate the fraction of tetrahedral voids occupied by Ag <sup>+</sup> ions.

**Ans**: Since zinc blende crystal has face-centerd cubic (*fcc*) unit cell, AgI is also a fcc crystal. Thus in AgCl crystal, I<sup>-</sup> ions have ccp arrangement and Ag<sup>+</sup> ions occup altternate out of 8 available tetrahedral voids. Thus :

Fraction of tetrahedral voids occupied by Ag<sup>+</sup> ions =  $\frac{4}{8} = \frac{1}{2} = 50\%$  (Ans.)

Q.9 The composition of a sample of wustile is Fe0.93O. What percentage of iron is present in the form of Fe (III)?

**Ans**: As a matter of fact the given compound,  $Fe_{0.93}O$  contains Fe as  $Fe^{2+}$  and  $Fe^{3+}$  ions. If the formula contains x atoms of  $Fe^{3+}$  ions, then the number of  $Fe^{2+}$  ions present in the formula would be equal to (0.93 - x). Hence the formula would be :

$$Fe^{2+}_{(0,93-x)} Fe^{3+}_x O^{2-}$$

Since the compound is neutral, the sum of charges should be equal to zero. Thus :

2(0.93 - x) + 3x - 2 = 0or 1.86 - 2x + 3x - 2 = 0

or x = 0.14

Thus the actual formula of the compound is :

$$Fe^{2+}_{(0.93 - 0.14)} Fe^{3+}_{0.14} O^{2-} \text{ or } Fe^{2+}_{0.79} Fe^{3+}_{0.14} O^{2-}$$

Molar mass of the compound =  $0.79 \times 56 + 0.14 \times 56 + 1 \times 16$ 

$$= 56 (0.79 + 0.14) + 16$$

$$= 56 \times 0.93 + 16$$

Weigth of Fe<sup>3+</sup> present in the compound =  $0.14 \times 56 = 7.84$  g

:. % of Fe present as Fe (III) =  $\frac{7.84}{68.08} \times 100\% = 11.5\%$  (Ans.)

Q.10 Why is diamond a bad conductor of electricity but a good conductor of heat.

Ans : Conduction of electricity essentially requires movement of electrons while conduction of heat does not necessarily require movement of electrons.

# Q.11 Make a comparison between hexagonal close packing (*hcp*) and cubic close packing (*ccp*) of spheres.

Ans : (A) Similarities. (i) In both the packings, each sphere (atom) is in direct contact with 6 other spheres in its own layer, 3 other spheres in the upper layer and 3 other spheres in the lower layer. Thus in these structures each sphere is in direct contact with 6 + 3 + 3 = 12 spheres. Hence C.N of each atom in these structures is equal to 12.

(ii) In both the structures, 74% of the available space is occupied by spheres. The remaining 26% of the space remains vacant, *i.e.* 26% of the space has voids or holes.

(B) Dissimilarities. (i) In hcp structure the different layers of atoms are packed in AB AB AB... patter. A layer has 7 spheres (atoms) and B layer contains 3 atoms. As a result, AB AB... pattern can also be represented as 73, 73... pattern. Here 7 and 3 represent the number of atoms present in A and B layers respectively. In ccp structure, different layers of atoms are packed in ABC ABC ABC... pattern. A layer has 1 atom, B and C both the layers have 6 atoms each. As a result ABC ABC... pattern can also be represent as 166, 166... pattern. Here 1, 6 and 6 represent the number of atoms in A, B and C layers respectively.

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(*ii*) In *hcp* structure, third layer of atoms covers the tetrahedral voids of the second layer. In *ccp* structure, third layer of atoms covers the octahedral voids of the second layer.

(*iii*) In *hcp* structure, third layer is similar to the first layer. Hence this structure has AB AB... arrangement. In *ccp* structure, every fourth layer is similar to the first layer and hence this structure has ABC ABC... arrangement.

#### Q.12 Determine the following :

(i) Number of ZnS units in a unit cell of zinc blende.

(ii) Number of CaF<sub>2</sub> units in a unit cell of fluorite.

(iii) Number of NaCl units in a unit cell of rock salt.

(iv) Number of CsCl units in a unit cell of CsCl crystal.

**Ans**: (i) The unit cell of zinc blende has ccp (or fcc) arrangement (or packing) of  $S^{2-}$  ions, *i.e.* in the unit cell of zinc blende  $S^{2-}$  ions are present on each of the 8 corners and on each of the six face centres. Unit cell of zinc blende has four  $Zn^{2+}$  ions within the body of the unit cell. Each  $Zn^{2+}$  ion is surrounded tetrahedrally by  $S^{2-}$  ions. Thus :

No. of  $Zn^{2+}$  ions in the unit cell of zinc blende

= 4 (within the body of the unit cell).

and,

No. of  $S^{2-}$  ions in the unit cell of zinc blende

 $= 8 \times \frac{1}{8} \text{ (corner S}^{2-} \text{ ions)} + 6 \times \frac{1}{2} \text{ (face-centred S}^{2-} \text{ ions)}$ = 1 + 3 = 4

 $\therefore$  Formoula :  $Zn_4S_4 \equiv 4 ZnS$ 

Obviously the number of ZnS units in the unit cell of zinc blende = 4.

(*ii*) The unit cell of fluorite has ccp (or fcc) arrangement of  $Ca^{2+}$  ions, *i.e.* in the unit cell of fluorite,  $Ca^{2+}$  ions are present on each of the 8 corners and one on each of the six face centres. Unit cell of fluorite also has eight F<sup>-</sup> ions within the body of the unit cell. Thus :

No. of  $Ca^{2+}$  ions in the unit cell of fluorite (CaF<sub>2</sub>)

$$= 8 \times \frac{1}{8} \text{ (corner Ca}^{2+} \text{ ions)} + 6 \times \frac{1}{2} \text{ (face-centered Ca}^{2+} \text{ ions)}$$
$$= 1+3=4$$

No. of  $F^-$  ions = 8 (within the body of the unit cell)

:. Formula :  $Ca_4F_8 \equiv 4CaF_2$ 

Obviously the unit cell of fluorite has four CaF<sub>2</sub> units.

(*iii*) The unit cell of rock salt has fcc arrangement (or packing) of  $Cl^-$  ions, *i.e.* in the unit cell of rock salt,  $Cl^-$  ions are present on each of 8 corners and one on each of the six face centres. Unit cell of rock salt also contains one Na<sup>+</sup> ion at its body centre and 12 Na<sup>+</sup> ions on 12 edge centres. Thus :

No. of Na<sup>+</sup> ions in the unit cell of rock salt

= 1 (body-centred Na<sup>+</sup> ion) +  $12 \times \frac{1}{4}$  (edge-centerd Na<sup>+</sup> ions), = 1 + 3 = 4

No. of Cl- ions in the cell of rock salt

$$= 8 \times \frac{1}{8} \text{ (corner Na^+ ions)} + 6 \times \frac{1}{2} \text{ (face-centerd Na^+ ions)}$$
$$= 1 + 3 = 4$$

 $\therefore$  Formula : Na<sub>4</sub>Cl<sub>4</sub> = 4NaCl

Obviously unit cell of rock salt has four NaCl units.

(iv) The unit cell of CsCl crystal has  $8Cl^-$  ions on eight corners of the unit cell and one Cs<sup>+</sup> ion of the body centre. Hence :

No. of Cl<sup>-</sup> ions present in unit cell =  $8 \times \frac{1}{8} = 1$ 

No. of  $Cs^+$  ions present in unit cell = 1 (in the body of the unit cell)

.: Formula : CsCl

Obviously the number of CsCl units in the unit cell of CsCl is 1.

#### Q.13 What are the diffirences between Schottky and Frenkel defects.

**Ans** : The main points showing the diffirences between these two types of defects are given in the following Table.

Table. Differences between sclottky and Frenkel defects.

Schottky defect	Frenkel defect
<ul> <li>(i) This defect is created when equal number of cations and anions are completely missing from their lattice sites.</li> </ul>	(i) This defect is created when ions (usually cations) leave their original sites and occupy the vacant interstial sites else where in ionic crystal.
( <i>ii</i> ) This defect decreases the density of ionic crystal.	( <i>ii</i> ) This defect does not change the density of the crystal.
( <i>iii</i> ) This defect does not change the dielectric constant value of ionic crystal.	( <i>iii</i> ) This defect increases the value of dielectric constant value of the crystal.
( <i>iv</i> ) This defect is shown by those ionic crystals in which C.N. of cations and anions is high and these ions have small diffirence in their size.	(iv) This defect is shown by those ionic crystals in which C.N. of cations and anions is low and these ions have large difference in their size.
(v) This defect is shown by alkali metal halides.	(v) Alkali metal halides do not show this defect.
(vi) Examples : NaCl, KCl, AgBr, CsCl.	(vi) Examples : AgCl, AgBr, AgI, Zns etc.

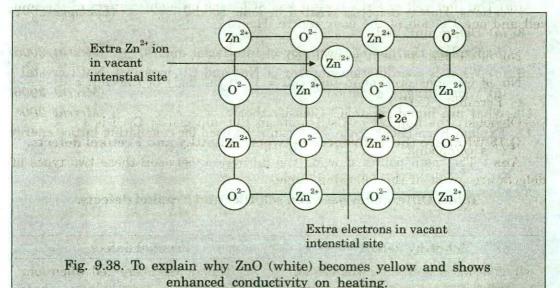
Structure of Solids

Q.14 ZnO is white but it turms yellow and shows enhanced electrical conductivity on heating. Explain.

Ans: When ZnO is heated, it loses  $O_2$  gas and  $Zn^{2+}$  ions are produced.

$$\operatorname{ZnO} \longrightarrow \operatorname{Zn}^{2+} + \frac{1}{2}\operatorname{O}_2 + 2e^{-}$$

 $Zn^{2+}$  ions thus produced occupy the vacant interstial sites and liberated electrons occupy the neighbouring vacant intesstial sites as shown in Fig. 9.38 so that the neutrality of ionic crystal (ZnO) may be maintained. It is due to the presence of electrons that white ZnO becomes yellow on heating and its electrical conductivity also increases.



**University Questions** 

- 1. (a) What is Born-Haber cycle? Explain how it is used for calculating lattice energy of NaCl?
- (b) What is the total number of ions in a unit cell of NaCl?

(Himachal Pradesh 2000)

2. Name important defects found in crystals. How are they caused ? What is the effect of these defects on the solubility of the crystals?

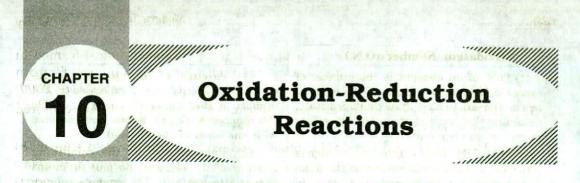
(Kanpur 2000)

- 3. Write a note on : (i) Radius ratio and its limitations (ii) Metallic bond (iii) Lattice energy. (Gauhati (General) 2000)
- 4. (a) Explain why metal excess non-stoichiometric compounds behave as semiconductors.

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- (b) Distinguish between octahedral and tetrahedral sites (holes) formed in closed-packed ionic solids. Derive the limiting radius ratio (r/r) for both these sites. (Lucknow 2000)
- 5. (i) Draw and explain the elements of symmetry present in a face centered cubic crystal.
  - (ii) Draw (100), (110) and (111) planes and explain interplaner distance. (8) (Bharathiar 2000)
- 6. What is lattice energy? How it is determined? (Lucknow 2001)
- 7. Based on the hard sphere model for the packing of ionic solids, relate the limiting radius ratio of cations and anions to the coordination number of cations. How a defect is created in ionic solids? (Lucknow 2001)
- 8. (a) Define unit cell.
  - (b) Explain the law of constancy of interfacial angles. (Meerut 2005)
- 9. (a) What is coordination number of Na<sup>+</sup> and Cl<sup>-</sup> ions in a NaCl crystal?
  (b) Write Bragg's equation. (Meerut 2006)
- 10. What are liquid crystals? Classify them. (Meerut 2008)
- 11. Explain Born-Hiber Cycle. How can it be used for calculating lattice energy of a compound.



### **Covalency, Oxidation Number and Oxidation State**

**Covalency** of an element represents (i) the number of H-atoms with which an atom of that element can combine (ii) the number of single bonds which an atom of that element can form (iii) the number of electrons its atom is able to share with other element. Thus in every case covalency of an element is a pure number and has no plus or minus sign associated with it. For example covalency of nitrogen in  $NH_3$  is 3.

**Oxidation number** of an element is defined as the formal charge which an atom of that element appears to have when electrons are counted. Oxidation number of an atom may be positive or negative. For example (i) oxidation number of K and Br in KBr is +1 and -1 respectively. (ii) Oxidation number of N in NH<sub>3</sub> is -3.

There may be a difference between the magnitude of covalency and oxidation number of the same element in various compounds. For example, in each of the following compounds, since C-atom shares four pairs of electrons with other atoms, the covalency of carbon is 4 while the oxidation number of carbon in these compounds is -4, -2, 0, +2 and +4 respectively.

Compound :	CH <sub>4</sub> Methane	CH <sub>3</sub> Cl Methyl chloride	CH <sub>2</sub> Cl <sub>2</sub> Methylene chloride	CHCl <sub>3</sub> Chloroform	CCl <sub>4</sub> Carbon tetra- chloride
Covalency of carbon	4	4	4	4	4
$\left. \begin{array}{c} \text{Oxidation} \\ \text{number of} \\ \text{carbon} \end{array} \right\}:$	- 4	-2	0	+ 2	+ 4

In ionic compounds the **oxidation state** of an element is the same as the charge on the ion formed from the atom of the element. For example in KBr, K is said to be in +1 oxidation state while Br is said to be in -1 oxidation state. Oxidation state of an element is its oxidation number of per atom. For example

the oxidation state of Al in  $Al_3O_3 = +6/2 = +3$ .

## Differences between Oxidation Number (O.N.) and Valency

The differences between oxidation number and valency has been shown in a tabular form as follows :

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Oxidation Number (O.N.)	Valency
(1) O.N. of an element is the number of excess charges that an atom of the element has or appears to have in its combined state, assuming that each electron belongs either to one or another atom.	(1) Valency of an element is its combining capacity and is expressed as the number of H-atoms or Cl atoms or double the number of oxygen atoms that combine with one atom of the element.
(2) With O.N. plus (+) or minus (-) sign is attached as it is the charge left on the atom of the element. For example O.N. of C in $CO = +2$ while O.N. of C in $CH_3Cl = -2$ .	(2) Since valency is the combining capacity of the element, no plus or minus sign is attached to it. For example valency of C is 4.
(3) O.N. of an element varies from compound to compound. <i>i.e.</i> O.N. of an element depends on the nature of the compound in which the element is present. For example O.N. of C in $CH_4$ , $C_2H_6$ , $C_2H_4$ , $C_2H_2$ and $CH_2Cl_2$ is -4, -3, -2, -1 and 0 respectively.	(3) Valency of an element is usually fixed. For example the valency of carbon in its compounds is 4, <i>i.e.</i> carbon is tetravalent in its compounds.
(4) O.N. of an element may be whole number or it may be fractional. For example O.N. of Mn in $Mn_3O_4$ is $+\frac{8}{3}$ .	(4) Valency of an element is always whole number and is never fractional. For example valency of Mn is 2.
(5) O.N. of an element can be zero. For example O.N. of carbon in $\mathrm{CH}_2\mathrm{Cl}_2$ is 0.	(5) Valency of an element is never zero (exception is noble gases), since it is the combining capacity of the element.

#### **Rules for Calculating Oxidation Number**

In order to calculate the oxidation number (O.N.) of an element in a given molecule/ion, the following rules are followed. These are arbitrary rules :

(i) The oxidation number of an element in the free or uncombined state is zero.

(ii) Fluorine, the most electronegative element, has an oxidation number of -1 in all its compounds.

(*iii*) The oxidation number of hydrogen is +1 in all its compound except in the ionic metal hydrides where its O.N. is -1. For example the O.N. of H in H<sub>2</sub>O is +1 while its O.N. in NaH is equal to -1.

(*iv*) The O.N. of oxygen is generally equal to -2 except in  $F_2O$  in which the O.N. of oxygen is equal to +2. In  $H_2O_2$  molecule whose Lewis structure is : $\ddot{O}$ .. $\ddot{O}$ : or : $\ddot{O}$ - $\ddot{O}$ :, the electron pair shared between H and O atoms is counted H H H H

with O-atom, since it is more electronegative than H-atom. Therefore the number of electrons counted with each O-atom is equal to seven instead of its outermost shell six electrons. Therefore O-atom in  $H_2O_2$ , molecule appears to have -1 charge on it, *i.e.* O.N. of O-atom in  $H_2O_2$  molecule (or its derivatives like  $BaO_2$  etc.) is equal to -1.

#### **Oxidation-Reduction Reactions**

(v) The net charge on a given ion is equal to the sum of the oxidation numbers of all the atoms present in the ion.

(vi) The oxidation number of a neutral molecule is always zero and is equal to the sum of oxidation numbers of the individual atoms, each multiplied by the number of atoms of the element in the molecule.

#### Solved Examples

The rules given above can be illustrated by studying the following solved examples.

**Example 1.** Calculate the oxidation number of (i) Cr in  $Na_2Cr_2O_7$  (ii) Mn in KMnO4 (iii) S in H2SO4.

#### Solution. (i) Cr in Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>

Let the oxidation number of Cr in  $Na_2Cr_2O_7$  be x

0.N. of Na = + 1; 0.N. of each 0 = 
$$-2$$

Putting the sum oxidation numbers equal to zero, we have :

$$2 \times 1 + 2x + [7 \times (-2)] = 0$$

or

$$x = +6$$

 $\therefore$  Oxidation number of Cr in Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> is +6.

(ii) Mn in KMnO<sub>4</sub>.

Let the oxidation number of Mn in  $KMnO_4$  be x

N. of 
$$K = +1$$
; O.N. of each O atom =  $-2$ 

Putting the sum of the oxidation numbers of the atoms in the compound equal to zero, we have :

$$4\times(-2)=0$$

or

: Oxidation number of Mn in  $KMnO_4$  is +7

1 + x +

(iii) S in H<sub>2</sub>SO<sub>4</sub>.

Let the O.N. of S in  $H_2SO_4$  be x

0.N. of each hydrogen = +1; 0.N. of each 0 atom = -2

2 + x + 4(-2) = 0

or

$$x = + 6$$

 $\therefore$  Oxidation number of S in H<sub>2</sub>SO<sub>4</sub> is + 6.

**Example 2.** Calculate the oxidation number of (i) Mn in  $MnO_4^-$  and  $MnO_4^{2-}$ ions (ii) Cr in  $Cr_2O_7^{2-}$  and  $CrO_2Cl_2$  (iii) S in  $S_2O_7^{2-}$ .

(Kanpur B.Sc. 1980; Maduarai 1975)

Solution. (i) Let the O.N. of Mn be x.

Now O.N. of each oxygen = -2.

 $\therefore$  In  $MnO_4^-$  ion :

or 
$$1 \times x + 4 \times (-2) = -1$$
  
 $x = +7$ 

or

 $\therefore$  O.N. of Mn in MnO<sub>4</sub><sup>-</sup> ion = +7 Similarly, in  $MnO_4^{2-}$  ion :  $1 \times r + 4 \times (-2) = -2$ x = +6or  $\therefore$  O.N. of Mn ion MnO<sub>4</sub><sup>2-</sup> ion = +6. (ii) Let the O.N. of Cr be x Now O.N. of each O-atom = -2O.N. of each Cl-atom = -1and :. In  $Cr_2O_7^{2-}$  ion :  $2 \times x + 7 \times (-2) = -2$ x = +6or  $\therefore$  ON. of Cr in Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> ion = +6 Similarly, in CrO<sub>2</sub>Cl<sub>2</sub> molecule :  $1 \times x + 2 \times (-2) + 2(-1) = 0$ x = +6or  $\therefore$  O.N. of Cr in CrO<sub>2</sub>Cl<sub>2</sub> = + 6. (*iii*) Let the O.N. of S be x $2 \times x + 7 \times (-2) = -2$ ... x = +6 $\therefore$  O.N. of S in S<sub>2</sub>O<sub>7</sub><sup>2-</sup> ion = +6.

or

#### **Oxidation and Reduction**

Oxidation is a reaction in which an atom or an ion loses one or more electrons and thus increases its valency, i.e. in oxidation the atomic or ionic system loses one or more electrons and is changed into more electropositive or less electronegative state. Due to the loss of electrons, oxidation is also called de-electronation.

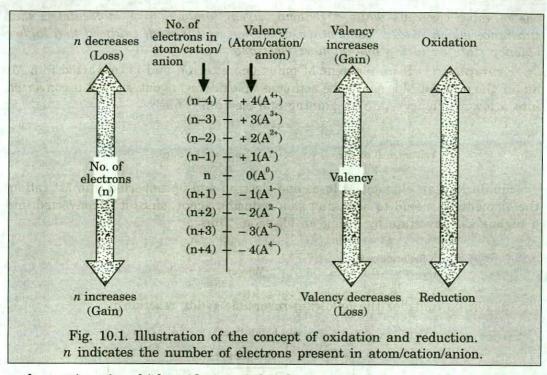
Reduction is a reaction in which an atom or an ion gains one or more electrons and thus decreases its valency, i.e. in reduction the atomic or ionic system gains one or more electrons and is changed into less electropositive or more electronegative state. Due to gain of electrons, reduction is also called electronation,

Illustration. The concept of oxidation and reduction has been illustrated in Fig. 10.1 in which n indicates the number of electrons present in atom/cation/ anion. When we proceed upwards from zero valency (Å), the number of electrons (n)goes on decreasing and hence oxidation takes place. Similarly on proceeding downwards from zero valency (Å), the number of electrons (n) goes on increasing and hence reduction takes place.

#### **Redox Reactions and Half Reactions**

Since loss or gain of electrons are relative terms, the gain or loss of electrons takes place simultaneously in a chemical reaction. Thus the oxidation (*i.e.* loss of electrons) and reduction (i.e. gain of electrons) reactions go hand in hand and

**Oxidation-Reduction Reactions** 



such reactions in which oxidation and reduction take place simultaneously are known as **oxidation-reduction reactions** or **redox reactions**. For example the reaction between Zn and  $CuSO_4$  solution shown as :

is a redox reaction, since Zn atom (valency = 0) by losing two electrons is oxidised to  $Zn^{2+}$  ion (valency = +2) while  $Cu^{2+}$  ion (valency = +2) by gaining the same number of electrons lost by Zn atom gets reduced to Cu atom (valency = 0).

Thus we see that a redox reaction consists of two reactions—one involves oxidation (e.g.  $Zn \rightarrow Zn^{2+} + 2e^{-}$ ) and the other involves reduction (e.g.  $Cu^{2+} + 2e^{-} \rightarrow Cu$ ). Each of these reactions is called **half reaction**. The reaction showing oxidation is called **oxidation half-reaction** while that representing reduction is called **reduction half-reaction**. Thus the two half-reactions of which the redox reaction (A) is composed of are :

and,

or

$$Zn \rightarrow Zn^{2+} + 2e^{-}$$
 ...(called oxidation half-reaction) ... (i)

 $Cu^{2+} + 2e^- \rightarrow Cu$  ...(called reduction half-reaction) ...(ii)

It may be noted that the number of electrons lost or gained in two opposite half-reactions of a redox reaction is equal and the reaction mixture of a redox reaction is electrically neutral.

## Oxidising Agent (Oxidant) and Reducing Agent (Reductant)

An oxidising agent (atom, ion or molecule) is that substance which oxidises some other substance, and is itself reduced to a lower valency state by gaining

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one or more electrons while a reducing agent (atom, ion or molecule) is that substance which reduces some other substance, and is itself oxidised to a higher valency state by losing one or more electrons.

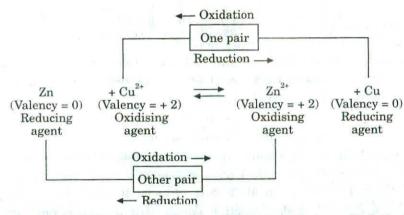
**Examples.** (1) If an element M gains one electron and is converted into  $M^-$  anion, the element M is said to be acting as an oxidising agent, since it is converted into a lower valency state by gaining one electron. Thus :

M	+ e <sup>-</sup>	$\rightarrow$	M-	
Oxidising agent				
[Valency = 0 (higher)]		Va	alency $= -1$ (lower	r
valency)]			valency)]	

Similarly if an element M loses one electron and is converted into  $M^+$  cation, the element M is said to be acting as a reducing agent, since it is converted into a higher valency state by losing an electron. Thus :

M	$\rightarrow$	$M^{+} + e^{-}$
Reducing agent [Valency = 0 (lower valency)]		Valency = +1 (higher valency)]

(2) Let us consider the following reversible redox reaction :



When we consider the left hand side of this reaction, we find that, since Zn metal reduces  $Cu^+$  ions to Cu metal and is itself oxidised to  $Zn^{2+}$  ion, Zn metal is said to be acting as a reducing agent. Now we can also say that  $Cu^+$  ion oxidises Zn metal to  $Zn^{2+}$  ion and is itself reduced to Cu metal and hence  $Cu^{2+}$  ion acts as an oxidising agent. Now when we consider the right hand side of the above reaction, we find that, since  $Zu^{2+}$  ion oxidises Cu metal to  $Cu^{2+}$  ion and is itself reduced to Zn metal.  $Zn^{2+}$  ion acts as an oxidising agent. Similarly since Cu metal reduces  $Zn^{2+}$  ion to Zn metal and is itself oxidised to  $Cu^{2+}$  ion, Cu metal acts as a reducing agent. On considering both the sides simultaneously we conclude that each side of a redox reaction consists of one oxidising and one reducing agent as written below each of the reactants and products.

The following points may be noted :

(i) The oxidising agent has higher oxidation state than its counter part reducing agent lying on the other side of the redox reaction. For example in the above redox reaction  $Cu^{2+}$  ion (oxidising agent) is in +2 oxidation state while Cu

## **Oxidation-Reduction Reactions**

(counter part reducing agent) is in zero oxidation state. Similarly  $Zn^{2+}$  ion (oxidising agent) is in +2 oxidation state while Zn (counter part reducing agent) is in zero oxidation state.

(ii) The oxidising agent is obtained when its counter part reducing agent loses electrons. Similarly a reducing agent is obtained when its counter part oxidising agent gains electrons. For example  $Zn^{2+}$  ion (oxidising agent) is obtained when Zn (counter part reducing agent) loses two electrons and Cu (reducing agent) is obtained when  $Cu^{2+}$  ion (counter part oxidising agent) gains two electrons.

## Equivalent Weights of Oxidising Agents

The equivalent weight of an oxidising agent (molecule or ion) is its that weight which can take up one electron, i.e. the equivalent weight of an oxidising agent is equal to its molecular weight or ion weight divided by the number of electrons gained by its per molecule or per ion.

**Examples.** (i) In the reduction of  $Fe^{3+}$  ion to  $Fe^{2+}$  ion as shown below :

$$\mathrm{Fe}^{3+} + e^- \rightarrow \mathrm{Fe}^{2+},$$

 $Fe^{3+}$  ion gains one electron and hence the equivalent weight of  $Fe^{3+}$  ion (oxidising agent) is equal to its ion-weight, *i.e.* equal to 56 gm. Accordingly the equivalent weight of  $FeCl_3$  in its reduction to  $FeCl_2$  is the same as its molecular weight.

(ii)  $\operatorname{Sn}^{4+}$  ion gains two electrons for its reduction to  $\operatorname{Sn}^{2+}$  ion.

$$\operatorname{Sn}^{4+} + 2e^- \to \operatorname{Sn}^{2+}$$

Hence the equivalent weight of  $\operatorname{Sn}^{4+}$  ion is half the ion-weight of  $\operatorname{Sn}^{4+}$  ion. Accordingly the equivalent weight of  $\operatorname{SnCl}_4$  is equal to half of its molecular weight.

(iii)  $MnO_4^-$  ion in its reduction to  $Mn^{2+}$  ion in acid solution gains five electrons

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$$

Thus the equivalent weight of  $MnO_4^-$  ion is one-fifth of its ion-weight, i.e. (54.9 + 64)/5 = 23.8 gms. Accordingly the equivalent weight of  $KMnO_4 = (39.1 + 54.9 + 64)/5 = 158.0/5 = 31.6$  gms.

(iv) The oxidation reaction of  $Cr_2O_7^{2-}$  in an acid solution proceeds with the gain of six electrons as shown :

$$Cr_2O_7^{2-} + 14H^+ 6e^- \rightarrow 2Cr^{3+} - 7H_2O$$

Consequently the equivalent weight of  $Cr_2O_7^{2-}$  ion is equal to  $(51.9 \times 2 + 16 \times 7)/6 = 35.9$  gms. Accordingly the equivalent weight of  $K_2Cr_2O_7$  is equal to  $(39 \times 2 + 51.9 \times 2 + 16 \times 7)/6 = 48.9$  gms.

## Equivalent Weights of Reducing Agents

On the basis of the similar arguments as used for oxidising agents, the equivalent weight of a reducing agent (molecule or ion) is its that weight which can loss one electron. i.e. the equivalent weight of a reducing agent is equal to its molecular weight or ion weight divided by the number of electrons lost by its per molecule or per ion. **Examples.** (i) Oxidation of  $Fe^{2+}$  ion to  $Fe^{3+}$  ion. The conversion of  $Fe^{2+}$  ion into  $Fe^{3+}$  ion is represented by :

Fe <sup>2+</sup>	$\rightarrow$	$Fe^{3+} + e^{-}$	
Reducing		Oxidising	
agent		agent	

Thus the equivalent weight of  $Fe^{2+}$  ion (which is a reducing agent in this reaction) is equal to its ion-weight.

(*ii*) **Oxidation of Sn<sup>2+</sup> ion to Sn<sup>4+</sup> ion.** The oxidation of Sn<sup>2+</sup> ion into Sn<sup>4+</sup> ion involves the loss of two electrons as shown below :

$Sn^{2+}$	$-2e^{-}$	$\rightarrow$	$Sn^{4+} + 2e^{-}$
Reducing			Oxidising
agent			agent

Thus the equivalent weight of  $\operatorname{Sn}^{2+}$  ion is equal to its ion-weight/2 because it loses two electrons to convert into  $\operatorname{Sn}^{4+}$  ion.

(iii) Oxidation of  $S_2O_3^{2-}$  ion to  $S_4O_6^{3-}$  ion. The equivalent weight of a  $S_2O_3^{2-}$  ion whose oxidation proceeds as follows :

$$2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2e^{-}$$

is equal to  $(2 \times \text{ion-weigh})/2$ , *i.e.* equal to its ion-weight. Hence equivalent weight of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>.5H<sub>2</sub>O is equal to its molecular weight, *i.e.* equal to 248.

It should be remembered that the equivalent weight of a particular oxidising agent is not a constant quantity. It may change depending on the nature of the oxidation-reduction reaction. For example, the oxidation reactions of  $\rm KMnO_4$  solution in acidic and alkaline medium are shown as :

 $\rm MnO_4^-$  + 8H^+ +5e^-  $\rightarrow \rm Mn^{2+}$   $\downarrow$  + 4H2O (Acidic medium)

 $MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 \downarrow + 4OH^- (Alkaline medium)$ 

The above reactions show that the equivalent weight of  $KMnO_4$  as an oxidising agent in acidic medium is equal to one-fifth of its molecular weight while its equivalent weight in alkaline medium is equal to one-third of its molecular weight.

### Auto-oxidation

There are substances like turpentine, olefinic compounds, phosphorus and some metals (e.g. Zn and Pb) which have a tendency to absorb  $O_2$  from the air and then become active. These active substances can oxidise other substances which are not normally oxidised by them. For example :

(i)  $H_2O$  in presence of lead is oxidised by air to  $H_2O_2$ .

$$Pb + O_2 + H_2O \rightarrow PbO + H_2O_2$$

(*ii*) When a dilute solution of KI mixed with a small amount of turpentine is allowed to stand in an open vessel, a small amount of  $H_2O_2$  is formed which is indicated by the liberation of  $I_2$ . If starch solution is added, it turns blue.

In both the examples given above the formation of  $H_2O_2$  by the oxidation of  $H_2O$  is called **auto-oxidation**.

**Explanation of auto-oxidation.** In order to explain the phenomenon of auto-oxidation, *Bach* suggested that the other substance is supposed to combine

#### Oxidation-Reduction Reactions

with  $O_2$  to form an unstable addition compound, called moloxide which then gives up oxygen. This oxygen is used up by  $H_2O$  to form  $H_2O_2$ . Bach called lead an **activator**, since it activated  $O_2$  to combine with  $H_2O$  to form  $H_2O_2$  and water was called an **acceptor**. Thus the formation of  $H_2O_2$  can be represented by the following mechanism :

 $\begin{array}{cccc} Pb & + & O_2 & \rightarrow & PbO_2 \\ Activator & & & & & \\ Moloxide & & \\ (unstable addition & \\ compound) \\ PbO_2 & \rightarrow & PbO + O \\ H_2O & + & O & \rightarrow & H_2O_2 \end{array}$ 

### Acceptor

The turpentine or other unsaturated compounds which act as activators are supposed to take up  $O_2$  molecule in the form of -O-O at the double bond position to form the unstable peroxide (moloxide).

$$RHC-CHR+O_2 \rightarrow RHC-CHR (Moloxide)$$

This moloxide gives up oxygen which is used up by  $H_2O$  molecule or any other acceptor. The bleaching and disinfecting action of terpentine are due to the formation of  $H_2O_2$ .

#### Induced Oxidation

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It has been observed that if a solution of  $Na_2SO_3$  is exposed to air, it gets oxidised to  $Na_2SO_4$ . But, if a solution of  $Na_2AsO_3$  is exposed to air, it does not get oxidised to  $Na_2AsO_4$ . However, if a solution of  $Na_2SO_3$  is mixed with that of  $Na_2AsO_3$  and then the mixture be exposed to air, both undergo oxidation.

 $Na_2SO_3 + Na_2AsO_3 + O_2 \rightarrow Na_2SO_4 + Na_2AsO_4$ 

Thus we see that  $Na_2SO_3$ , while undergoing oxidation on exposure to air, also brings about oxidation of  $Na_2AsO_3$  which itself cannot oxidise when exposed to air. Thus :

The phenomenon in which one substance while undergoing oxidation itself on exposure to air brings about oxidation of another substance also which of itself cannot take up oxygen is known as induced oxidation.

**Explanation of induced oxidation.** Induced oxidation can be explained by Brodie's theory and by Bach's theory.

(a) Brodie's theory. According to this theory  $H_2O_2$  is formed which brings about the oxidation of  $Na_2AsO_3$  to  $Na_2AsO_4$ .

$$\begin{array}{rcl} \mathrm{Na_2SO_3} + \mathrm{O_2} + \mathrm{H_2O} &\rightarrow \mathrm{Na_2SO_4} + \mathrm{H_2O_2} \\ \mathrm{Na_2AsO_3} + \mathrm{H_2O_2} &\rightarrow \mathrm{Na_2AsO_4} + \mathrm{H_2O} \\ \end{array}$$
$$\begin{array}{rcl} \mathrm{Na_2SO_3} + \mathrm{Na_2AsO_3} + \mathrm{O_2} &\rightarrow \mathrm{Na_2SO_4} + \mathrm{Na_2AsO_4} \end{array}$$

(b) Bach's theory. The theory is based on the formation of moloxide (See autooxidation) by the reaction between  $Na_2SO_3$  and  $O_2$ .

$$\begin{array}{rcl} \mathrm{Na_2SO_3} + \mathrm{O_2} & \rightarrow & \mathrm{Na_2SO_5} \\ & & \mathrm{Moloxide} \end{array} \\ \mathrm{Na_2SO_5} + \mathrm{Na_2AsO_3} & \rightarrow & \mathrm{Na_2SO_4} + \mathrm{Na_2AsO_4} \end{array}$$
$$\begin{array}{rcl} \mathrm{Na_2SO_3} + \mathrm{Na_2AsO_3} + \mathrm{O_2} & \rightarrow & \mathrm{Na_2SO_4} + \mathrm{Na_2AsO_4} \end{array}$$

## Balancing Redox Equations by Oxidation Number Method.

This method is based on the principle that any increase in oxidation number must be compensated by a decrease. This method consists of the following steps :

(i) Note the elements which undergo change in oxidation numbers.

(ii) Select the suitable coefficients for the oxidising and reducing agents so that the total decrease in oxidation number of the oxidising agent becomes equal to the total increase in the oxidation number of the reducing agent.

### Solved Examples

The following examples illustrate the above method.

**Example 1.** Balance the following equation by oxidation number method :

 $CuO + NH_3 \rightarrow Cu + N_2 + H_2O$ 

**Solution.** The given equation shows that the oxidation number (O.N.) of Cu decreases from +2 (in CuO) to 0 (in Cu) while that of N increases from -3 (in NH<sub>3</sub>) to 0 (in N<sub>2</sub>) and hence :

$$\begin{array}{cccc} CuO &+ & NH_3 & \longrightarrow & Cu &+ & N_2 &+ & H_2O \\ (Cu = + 2) & (N = - 3) & (Cu = 0) & (N = 0) \\ & & & \\ & & & \\ \hline & & & \\ Decrease in & O.N. = 2 - 0 = 2 \\ \hline & & & \\ \hline & & & \\ \hline & & & \\ Reduction) \\ \hline & & & \\ Increase in & O.N = 0 - (-3) \\ & & = 3 \\ \hline & & \\ \hline & & \\ Oxidation) \end{array}$$

In order to equalise the total increase in O.N. (= 3) to the total decrease in O.N. (= 2), we should have three atoms of Cu for every two atoms of N and hence the equation should be written as :

$$3CuO + 2NH_3 \rightarrow 3Cu + N_2 + H_2O$$

Now in order to balance O-atoms we should add  $3H_2O$  molecules to the right hand side. Thus :

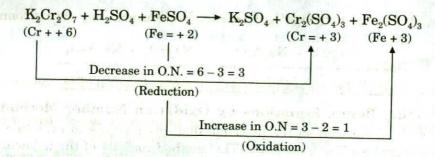
 $3CuO + 2NH_3 \rightarrow 3Cu + N_2 + 3H_2O$ 

This is the balanced equation.

Example 2. Balance the following equation by oxidation number method.

 $\begin{array}{l} \mathrm{K_2Cr_2O_7} + \mathrm{H_2SO_4} + \mathrm{FeSO_4} \rightarrow \mathrm{K_2SO_4} + \mathrm{Cr_2(SO_4)_3} + \mathrm{Fe_2(SO_4)_3} \\ & (Lucknow \ B.Sc. \ 1981) \end{array}$ 

**Solution.** The given equation shows that O.N. of Cr decreases from  $+6(in K_2Cr_2O_7)$  to  $+3 [in Cr_2(SO_4)_3]$  while that of Fe increases from  $+2 (in FeSO_4)$  to  $+3 [in Fe_2(SO_4)_3]$  and hence :



In order to equalise the total increase in O.N. (= 1) to the total decrease in O.N. (= 3) we should have one atom of Cr for every three atoms of Fe or two atoms of Cr for every six atoms of Fe and hence above equation should be written as :

 $\mathrm{K_2Cr_2O_7} + \mathrm{H_2SO_4} + \mathrm{6FeSO_4} \rightarrow \mathrm{K_2SO_4} + \mathrm{Cr_2(SO_4)_3} + \mathrm{Fe_2(SO_4)_3}$ 

In order to balance Fe atoms we should write the above equation as :

 $\mathrm{K_2Cr_2O_7} + \mathrm{H_2SO_4} + \mathrm{6FeSO_4} \rightarrow \mathrm{K_2SO_4} + \mathrm{Cr_2(SO_4)_3} + \mathrm{3Fe_2(SO_4)_3}$ 

Now in order to balance O-atoms we add  $7H_2O$  molecules to the right hand side and to balance H-atoms we write  $7H_2SO_4$  in place of  $H_2SO_4$  on the left hand side. Thus the equation in its balanced form becomes :

 $\rm K_2Cr_2O_7$  + 7H\_2SO\_4 + 6FeSO\_4  $\rightarrow \rm K_2SO_4$  +  $\rm Cr_2(SO_4)_3$  + 3Fe\_2(SO\_4)\_3 + 7H\_2O Balancing Redox Equations by Ion-electron Method—By the Use of Half-reactions

This method was developed in 1927 by Jatte and Lamer and various steps involved in the method are as follows :

(i) Break up the complete equation in two half reactions, one for the change undergone by the reducing agent and the other for the change undergone by the oxidising agent.

(ii) Balance each half reaction as to the number of atoms of each element. For this purpose :

(a) Balance the atoms other than H and O for each half-reaction by using simple multiples.

(b) In *neutral* and *acid* solutions,  $H_2O$  and  $H^+$  are added for balancing oxygen and hydrogen atoms. First balance the oxygen atoms. For each excess oxygen atom on one side of the equation, add one  $H_2O$  to the other side. Now use  $H^+$  to balance hydrogen atoms.

In alkaline solutions,  $OH^-$  may be used. For each excess on one side, balance is secured by adding one  $H_2O$  to the same side and  $2H^-$  to the other side. If hydrogen is still unbalanced, balance is secured by adding one  $OH^-$  for each excess hydrogen on the same side as the excess and one  $H_2O$  to the other side.

(iii) Equalise the charges on both sides by adding electrons to the side deficient in negative charges.

(iv) Multiply one or both half-reactions by a suitable number so that on adding the two equations, the electrons are balanced.

...(i)

(v) Add the two balanced half reactions and cancel any terms common to both sides. Also see that all electrons cancel.

#### Solved Examples

Various steps of the ion-electron method can be illustrated by considering the following examples :

Example 1. Balance the following redox reaction by ion-electron method :

 $\mathrm{Fe}^{2+}$  +  $\mathrm{MnO_4^-}$  +  $\mathrm{H^+} \rightarrow \mathrm{Mn^{2+}}$  +  $\mathrm{Fe^{3+}}$  +  $\mathrm{H_2O}$ 

(Udaipur B.Sc. 1978; Kanpur 1980)

Solution. Obviously the given redox reaction takes place in acidic medium and can be broken into the following two half-reactions :

 $\begin{array}{rcl} MnO_4^{-} & \rightarrow & Mn^{2+} & \dots & Reduction \ half \ reaction \\ (Mn = +7) & (Mn + 2) \\ & Fe^{2+} & \rightarrow & Fe^{3+} & \dots & Oxidation \ half \ reaction \end{array}$ 

and

For reduction half-reaction. (i) For balancing O-atoms add  $4H_2O$  to right hand side to get :

 $MnO_4^- \rightarrow Mn^{2+} + 4H_2O$ 

(ii) For balancing H-atoms add 8H<sup>+</sup> to the left hand side to get :

 $MnO_4^- + 8H^+ \rightarrow Mn^{2+} + 4H_2O$ 

(Fe = +2) (Fe = +3)

(iii) For balancing the charges add  $5e^-$  to the left hand side to get :

 $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ 

For oxidation half-reaction. Balance the charges on both sides by adding  $1e^{-}$  to the left hand side to get :

$$Fe^{2+} \rightarrow Fe^{3+} + e^{-}$$
  
 $5Fe^{2+} \rightarrow 5Fe^{3+} + 5e^{-}$ ....(*ii*)

or

On adding equations (i) and (ii), we get

 ${\rm MnO_4^-}$  + 8H<sup>+</sup> + 5Fe<sup>2+</sup>  $\rightarrow$  Mn<sup>2+</sup> + 4H<sub>2</sub>O + 5Fe<sup>3+</sup>

which is the balanced equation.

**Example 2.** Balance the following equation by using ion-electron method :  $Cr_2O_7^{2-} + Fe^{2+} + H^+ \rightarrow Cr^{3+} + Fe^{3+} + H_2O$ 

(Mysore B.Sc. 1980; Kanpur 1980; Raj. 1975; Udaipur 1981)

Solution. Obviously the given redox reaction takes place in acidic medium and can be broken into the following two half-reactions :

 $\begin{array}{rcl} {\rm Cr_2O_7}^{2-} & \rightarrow & {\rm Cr^{3+}} & \dots..Reduction \ half \ reaction \\ {\rm (Cr = +6)} & {\rm (Cr = +3)} \\ & {\rm Fe^{2+}} & \rightarrow & {\rm Fe^{3+}} & \dots..Oxidation \ half-reaction \\ {\rm (Fe = +2)} & {\rm (Fe = +3)} \end{array}$ 

For reduction half-reaction. (i) Balance the atoms other than oxygen and hydrogen

 $Cr_2O_7^{2-} \rightarrow 2Cr^{3+}$ 

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(*ii*) For balancing O-atoms add  $7H_2O$  to the right hand side to get :  $Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + 7H_2O$ 

(iii) For balancing H-atoms add 14H<sup>+</sup> to the left hand side to get :  $Cr_2O_7^{2-} + 14H^+ \rightarrow 2Cr^{3+} + 7H_2O$ 

(iv) For balancing the charges add  $6e^-$  to the left hand side to get :

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$

For oxidation half-reaction. Balance the charges on both the sides by adding  $1e^{-}$  to right hand side to get :

$$Fe^{2+} \rightarrow Fe^{3+} + e^{-}$$

 $6Fe^{2+} \rightarrow 6Fe^{3+} + 6e^{-}$ 

On adding equations (i) and (ii), we get :

 $Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O_2^{-1}$ 

This is the equation in its balanced form.

## **Questions with Answers**

Q.1 Explain the following reactions :

(i) Disproprotionation reactions (ii) Comproprotionation reactions, giving examples.

Ans: (i) Disproprotionation reactions. These reactions are also called *self* oxidation-reducation or self redox reactions. A reaction in which the same speciec is simultaneously oxidised as well as reduced is called a diproprotionation reaction. For such redox reactions to occur, the reacting species must contain an element which has at least three oxidation states. The element in the reacting species is present in the intermediate oxidation state while the higher and lower oxidation states are available for reduction and oxidation to occur.

**Examples.** Examples of disproprotionation reactions are given below.

(a) 
$$2NO_2(g) + 2OH^-(aq) \rightarrow NO_2^-(aq) + NO_3^-(aq) + H_2O(l)$$
  
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This is a disproprotionation reaction since here the oxidation state of nitrogen decreases from + 4 in NO<sub>2</sub> to + 3 in NO<sub>2</sub><sup>-</sup> ion, as well as increases from + 4 in NO<sub>2</sub> to 5 in NO<sub>3</sub><sup>-</sup> ion.

(b) The decomposition of hydrogen peroxide  $(H_2O_2)$  is a disproprotionation reaction where oxygen atom undergoes disproprotionation.

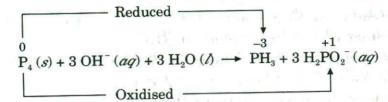
$$\begin{array}{c} & \overset{-\mathrm{Reduced}}{\longrightarrow} \\ 2\mathrm{H}_{2}\mathrm{O}_{2}\left(aq\right) \xrightarrow{-2} 0 \\ \mathrm{H}_{2}\mathrm{O}\left(l\right) + \mathrm{O}_{2}\left(g\right) \\ & & & \\ &$$

...(i)

...(ii)

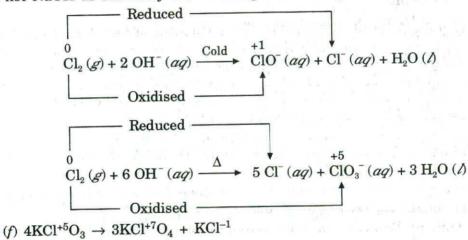
In the above reaction, the O.N. of oxygen which is -1 in  $H_2O_2$  increases to zero in  $O_2$  and decreases to -2 in  $H_2O$ .

(c) Phosphorus  $(P_4)$  undergoes disproprotional in alkaline medium as shown below.



(d) Sulphur  $(S_8)$  undergoes disproprotionation reaction in alkaline medium.

(e)  $Cl_2$  undergoes disproprotionation reaction in presence of dil. cold NaOH and hot NaOH as shown by the following chemical equations.



(g)  $2Cu^+ \rightarrow Cu^0 + Cu^{2+}$ 

(ii) Comproprotionation reactions. Comproprotionation reaction is the reverse of disproprotionation reaction, *i.e.* in comproprotionation reaction two same species in different oxidation states combine together to form a species which has intermediate oxidation state. For example :

$$Ag^{2+}(aq) + Ag^{\circ}(s) \rightarrow 2Ag^{+}(aq)$$

This reaction can be written as :

$$\begin{array}{c} & \text{Reduction} & & \\ & \text{Ag}^{2+}(aq) + \text{Ag}^{0}(s) & \longrightarrow & \text{Ag}^{+}(aq) + & \text{Ag}^{+}(aq) \\ & (\text{Ag} = 2) & (\text{Ag} = 0) & (\text{Ag} = +1) & (\text{Ag} = +1) \\ & & & & \\ & & & \\ & & & & \\$$

**Oxidation-Reduction Reactions** 

## Q.2 Explain why $F_2$ does not undergo disproprotionation reaction.

Ans: Since F is the most electronegative element, it shows only -1 O.S. in its compounds. It does not show any O.S. less than -1 and greater than -1 and hence it does not undergo disproprotionation reaction.

Q.3 Determine oxidation state of :

(i) C-atom in carbon suboxide  $(C_3O_9)$ .

(ii) Br-atom in tribromo octaoxide (Br<sub>3</sub>O<sub>8</sub>).

(*iii*) S-atom in tetrathionate ion  $(S_4O_6^{2-})$ .

(iv) Fe-atom in magenetic oxide (Fe<sub>3</sub>O<sub>4</sub>).

(v) Mn-atom in Mn<sub>3</sub>O<sub>4</sub>.

(vi) Pb atom in red lead (Pb<sub>3</sub>O<sub>4</sub>).

(vii) O-atom in KO<sub>3</sub>.

## (viii) Fe-atom in ferriferrocynide molecule, Fe4[Fe (CN)6]3.

(ix) F-atom in Fe<sub>0.4</sub>O.

Ans : (i) O.S. of C-atom in carbon suboxide,  $C_3O_2$ . The structure of  $C_3O_2$  (carbon suboxide) is :

$$-2 +2 0 +2 -2$$
  
 $0 = C = C = C = 0$ 

Since a double bond is formed by mutual sharing of two electrons and since oxygen is more electronegative than carbon, each of the two terminal oxygen atoms have an oxidation state of -2 and the carbons to which they are attached have an oxidation state of +2.Furthur, since whenever a covalent bond is formed between similar atoms, each of the atoms is given an oxidation state of zero. Therefore O.S. of the central carbon atom in  $C_3O_2$  is zero.

Thus, the two carbon atoms are present in + 2 oxidation state each, whereas the third one is present is zero oxidation state. Therefore, the average oxidation state of carbon in  $C_3O_2 = (2 \times 2 + 1 \times 0) / 3 = 4/3$ . (Ans.)

However, in reality, the terminal carbon atoms have an oxidation state of +2 while the middle carbon has an oxidation state of zero.

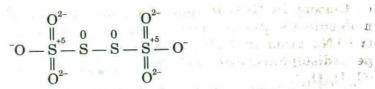
(*ii*) **O.S. of Br-atom in tribromoocta oxide**,  $Br_3O_8$ . The structure of tribromooctaoxide ( $Br_3O_8$ ) is :

 $0 \stackrel{0}{=} \stackrel{6}{\operatorname{Br}} \stackrel{0}{-} \stackrel{0}{\operatorname{Br}} \stackrel{0}{-} \stackrel{0}{\operatorname{Br}} \stackrel{0}{=} 0$ 

Following the arguments discussed under  $C_3O_2$ , we can easily find out that terminal bromine atoms are present in + 6 oxidation state while the middle one has an oxidation state of + 4. Thus the average oxidation number of Br in  $Br_3O_8$  turns out to be [2 (+ 6) + (+ 4)/3 = 16/3. (Ans)

(iii) O.S. of S-atom in tetrathionate ion,  $S_4O_6^{-2}$ . The structure of  $S_4O_6^{-2}$  ion is :

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Since each of the two terminal sulphur atoms is connected to two oxygen atoms by a double bond and to one oxygen atom by a single bond, the oxidation state of each of these terminal sulphur atoms is + 5. Since two central sulphur atoms are linked to each other by a single bond and each sulphur is furthur attached to similar species on either side, the electron pair forming the S - Sbond remains in the centre and hence each of the two central sulphur atoms has an oxidation state of zero. Thus, the average oxidation state of the four sulphur atoms is  $(2 \times 5 + 2 \times 0)/4 = 2.5$  (Ans)

(*iv*) **O.S. of Fe in magnetic oxide, Fe\_3O\_4.**  $Fe_3O_4$  is known to be a mixture of FeO and  $Fe_2O_3$  having the composition FeO.  $Fe_2O_3$ . Therefore, oxidation number of Fe in FeO is + 2 while in  $Fe_2O_3$  it is + 3. The average value, however, is [1 (+ 2) + 2 (+ 3)]/3 = 8/3 (Ans)

(v) **O.S. of Mn in Mn\_3O\_4.**  $Mn_3O_4$  is regarded as a mixture of MnO and  $MnO_2$  having the composition,  $2MnO.MnO_2$ . Therefore, the oxidation state of Mn in MnO is + 2 while that is  $MnO_2$  it is + 4. The average is [2 (+ 2) + (+ 4)]/3 = 8/3 (Ans)

(vi) **O.S. of Pb in red lead, Pb\_3O\_4.**  $Pb_3O_4$  is considered to be a mixture with the composition 2PbO. PbO<sub>2</sub>. Therefore, the oxidation state of Pb in PbO is + 2 while in PbO<sub>2</sub>, it is + 4. Here, again the average value [2 (+ 2) + 1 (+ 4)]/3 = 8/3. (Ans)

(vii) **O.S. of O-atom in KO<sub>3</sub>**. Let the oxidation state of O-atom in KO<sub>3</sub> be x. Hence :

$$(+1) \times 1 + 3 \times x = 0$$

x = -1/3 (Ans)

-

(viii) O.S. of Fe atom in  $Fe_4[Fe(CN)_6]_3$ . In  $Fe_4[Fe(CN)_6]_3$  four Fe atoms are in + 3 O.S. and three Fe atoms are in + 2 O.S. Thus the overage O.S. of Fe atom.

$$\frac{4\times(+3)+3\times(+2)}{7} = \frac{18}{7}$$
 (Ans.)

(ix) O.S. of Fe-atom in  $Fe_{0.94}O$ . O.S. of Fe (x) in  $Fe_{0.94}O$  is given by :

 $x \times \text{No. of Fe atoms} + (-2) \times \text{No. of O-atoms} = 0$ 

or

or

 $x \times 0.94 + (-2) \times 1 = 0$ 

or

or x = 2/0.94 = 2.12 (Ans)

0.94x = 2

Q.4 Calculate oxidation state of : (i) S-atom in Caro's acid or peroxomono sulphuric acid molecule ( $H_2SO_5$ ). (ii) N-atom in  $NH_4NO_3$ . (iii) Cr-atom in  $CrO_5$ . (iv) N-atom in  $NO_3$  ion. (v) Cl-atoms in bleaching powder molecule (CaOCl<sub>2</sub>). (vi) Fe-atom in K<sub>4</sub> [Fe(CN)<sub>6</sub>]. (vii) C-atom in HCN. (viii) C-atom in HNC. (ix) S-atom in oleum molecule ( $H_2S_2O_7$ )

#### **Oxidation-Reduction** Reactions

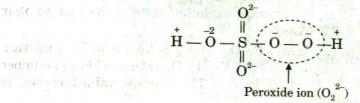
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(x) C-atom in HCOOH molecule. (xi) S-atom in sodium thiosulphate molecule (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>). (xii) S-atom in sodium tetrathionate (Na<sub>2</sub>S<sub>4</sub>O<sub>6</sub>). (xiii) Na atom in NaHg amalgam. (xiv) S-atom in Marshall's acid or peroxdisulphuric acid molecule ( $H_2S_2O_8$ ). (xv) C-atom in sucrose molecule  $(C_{12}H_{22}O_{11}).$ 

Ans. (i) By conventional method, the O.N. of S (x) in H<sub>2</sub>SO<sub>5</sub> is given by :

2(+1) + x + 5(-2) = 0 or x = +8

This is impossible because the maximum O.N. of S cannot be more than six since it has only six electrons in the valence shell. This fallacy is overcome if we calculate the O.N. of S by chemical bonding method.



 $2 \times (+1) + x + 2 (-1)$ +  $3 \times (-2) = 0$ or x = +6(for H) (for S) for (O - O) (for other O atoms)

(ii) Oxidation numbers of two N atoms in  $NH_4NO_3$  are different.  $NH_4NO_3$  is made of NH4+ and NO3-

In NH<sub>4</sub><sup>+</sup> ion, x + 4 (+ 1) = + 1  $\therefore$  O.N. of N is -3In NO<sub>3</sub><sup>-</sup> ion x + 3 (-2) = -1 : O.N. of N is + 5 Average O.S of N-atom = +5 + (-3)

.x. ad .O.Z. ni main O.M. and in = + 1 (Ans.)

(iii) According to conventional method, O.N. of Cr atom (x) in  $CrO_5$  molecule is given by.

 $x + 5 x (-2) = 0, \quad \therefore \quad x = + 10$ 

This is impossible because the maximum O.N. of Cr cannot be more than six since it has  $3 d^5 4s^1$  outer orbital configuration.

The correct value of O.N. of Cr atom is calculated with the help of the structure of CrO5 given below :

This structure shows that the value of x is given by :

 $x + 2 \times (-2) + 1 \times (-2) = 0$ Due to two Due to one peroxide ions oxide ion (O<sup>2-</sup>) x - 4 - 2 = 0 or x = +6 (Ans.) (iv) According to conventional method, O.N. of N is  $NO_3^- = x + 3 (-2) = -1$ or x = +5

According to chemical bonding method,  $O - N < O^2$ 

Thus, there is no fallacy about the O.N. of N in  $NO_3^-$  whether one calculates by conventional method or by chemical bonding method.

(v)  $CaOCl_2$  is made of  $Ca^{2+}$ ,  $OCl^-(Cl = +1)$  and  $Cl^-(Cl = -1)$ . Hence O.N. of two Cl atoms in  $CaOCl_2$  are + 1 and - 1 respectively.

(vi) In  $K_4[Fe(CN)_6]$  the individual O.N. of C and N are not known but for calculating O.N. of Fe, the sum of O.N. of C and N in  $(CN)^-$  unit is taken to be -1. Thus, O.N. of Fe is calculated as 4 (+1) + x + 6 (-1) = 0 or x = +2. (Ans)

(vii) The structure of HCN molecule is  $H-C \equiv N$ . Since N-atom in more electronegative than C-atom, each C - N covalent bond gives in O.S. of -1 to N-atom, Now since there are three C - N covalent bonds in HCN molecule, O.S.

of N-atom = -3. Hence HCN can be represented as  $\stackrel{+1}{H} \stackrel{x}{\longrightarrow} \stackrel{-3}{C} \equiv \stackrel{-3}{N}$ . Hence  $(+1) \times 1$ +  $x \times 1 + (-3) \times 1 = 0$  or x = +2 (Ans)

(*viii*) The structure of HNC molecule is  $H - N \cong C$ . Since N-atom (donor atom) is more electronegative than C-atom (accepter atom), O.S. of N-atom = -3. Thus

HNC can be represented as  $H \longrightarrow N \stackrel{-3}{\cong} C$ . Hence  $(+1) \times 1 + (-3) \times 1 + x \times 1 = 0$ or x = +2 (Ans)

(ix) The structure of  $H_2S_2O_7$  molecule is given below :

		$O^{2-}$		$O^{2-}$		
+1	2-	11 -	2-	_	2-	+1
H	- 0 -	$-\mathbf{S}^{x}$	-0-	$-\mathbf{S}^{x}$	-0-	-H
		1		1		
		$0^{2-}$		$0^{2}$		

In this structure since both S-atoms have identical chemical bonding, they have the same oxidation state which is equal to + 6 as shown below :

 $2 \times x + (-2) \times 7 + 2 \times (+1) = 0$ 

2x - 14 + 2 = 0,  $\therefore x = +12/2 = + 6$  (Ans)

(x) Since HCOOH molecule contains C, H and O, O.S. of C-atom (x) in this molecule can be calculated by using the formula :

No. of H-atoms  $\times$  O.S. of H-atom + No. of O-atoms  $\times$  O.S. of O-atom + No. of C-atoms  $\times$  O.S. of C-atom = 0

Hence in case of HCOOH molecule the above relation can be written as :

$$2 \times (+1) + 2 \times (-2) + 1 \times x = 0$$

$$x = +2$$
 (Ans

or

#### **Oxidation-Reduction Reactions**

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(xi) Conventional method gives O.S. to S-atom in  $Na_2S_2O_3$  molecule = + 2 as shown below :

$$2 \times (+1) + 2x + 3 \times (-2) = 0$$
  
(Due to Na) (Due to O)  
 $x = +2$ 

This oxidation state (= + 2) is wrong since the two S-atom in Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> molecule are in different oxidation states because of the fact that when Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> is heated with dil. H<sub>2</sub>SO<sub>4</sub>, one S-atom gets precipated and the other S-atom is converted into SO<sub>2</sub>. The correct O.S. of S-atom can be calculated from the structure of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> which is given below.

$$\overset{2}{\operatorname{Na}} \overset{2}{\operatorname{O}} \overset{-}{\operatorname{S}} \overset{-}{\operatorname{O}} \overset{-}{\operatorname{Na}} \overset{2}{\operatorname{O}} \overset{+}{\operatorname{Na}} \overset{2}{\operatorname{O}} \overset{+}{\operatorname{Na}} \overset{-}{\operatorname{O}} \overset{+}{\operatorname{Na}} \overset{+}{\operatorname{O}} \overset{-}{\operatorname{Na}} \overset{+}{\operatorname{O}} \overset{-}{\operatorname{O}} \overset{+}{\operatorname{Na}} \overset{+}{\operatorname{O}} \overset{-}{\operatorname{Na}} \overset{+}{\operatorname{O}} \overset{+}{\operatorname{Na}} \overset{+}{\operatorname{O}} \overset{+}{\operatorname{O}} \overset{+}{\operatorname{Na}} \overset{+}{\operatorname{Na}} \overset{+}{\operatorname{O}} \overset{+}{\operatorname{Na}} \overset{+}{\operatorname{Na}} \overset{+}{\operatorname{O}} \overset{+}{\operatorname{Na}} \overset{+}{\operatorname$$

In the structure given above each of the two Na atoms has an O.S. = +1, each of three O-atoms has O.S. = -2. Terminal S-atom has O.S. = -2. Let the O.S. of the central S-atom be x. Thus :

$$+2-6-2+x=0, \therefore x=+6$$

Thus :

...

O.S. of terminal S-atom = -2O.S. of central S-atom = +6 (Ans)

Average O.S. of S-atom = 
$$\frac{1 \times (-2) + 1 \times (+6)}{2}$$

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

(xii) The structure of  $Na_2S_4O_6$  molecule is given below :

$$\begin{array}{cccc} & O^{-2} & O^{-2} \\ & O^{-2} & O^{-2} \\ & NaO - S - S - S - S - S - S \\ & 0 \\ & 0^{-2} & O^{-2} \end{array}$$

In this structure each of the two central S-atoms which are linked together has O.S. = 0. Let the O.S. of each of the two remaining S-atoms be x. Hence :  $2 \times (+1) + 6 \times (-2) + 2 \times 0 + 2 \times x = 0$ 

(For Na atoms) (For O-atoms) (For central S-atoms)

$$+2 - 12 + 0 + 2x = 0$$

Thus :

...

O.S. of each central S-atom = 0

In this structure each of the two H-atoms has O.S. = -1, each of the six terminal O-atoms has O.S. = -2. This structure has one peroxide ion  $(O_2^{-2})$  whose O.S. = -2. In this ion each O-atom has O.S. = -1. Thus :

 $2 \times (+1) + 6 \times (-2) - 2 + 2x = 0$ (Due to H-atoms) (Due to six O-atoms) (Due to peroxide ion, O<sub>2</sub><sup>-2</sup>)  $\therefore x = + \frac{12}{2} = + 6 \text{ (Ans)}$ 

(xv) Since the given molecule  $(C_{12}H_{22}O_{11})$  contains H, C and O, O.S. of C-atom (x) is given by :

or

 $\begin{array}{l} x \times n_{\rm C} + (-2) \times n_{\rm O} + (+1) \times n_{\rm H} = 0 \\ x \times 12 + (-2) \times 11 + (+1) \times 22 = 0 \end{array}$ 

or

...

12x - 22 + 22 = 0

x = 0 (Ans)

**Q.5 Find out the formal charge on each O-atom in phosphate ion. Ans :** We know that phosphate ion is  $PO_4^{3-}$ . Formal charge on each O-atom in  $PO_4^{3-}$  ion

 $= \frac{\text{Total number of charges on PO}_{4}^{3-} \text{ ion}}{\text{Total number of O-atoms in PO}_{4}^{3-} \text{ ion}}$  $= \frac{-3}{4} = -0.75 \text{ (Ans.)}$ 

Q.6 Arrange the following species in the increasung order of oxidation state of the atom shown in parenthesis.

(a)  $SO_3^{2-}$ ,  $S_2O_4^{2-}$ ,  $S_2O_6^{2-}$  (S-atom)

(b) OF<sub>2</sub>, KO<sub>2</sub>, BaO<sub>2</sub>, O<sub>3</sub> (O-atom)

(c) KO<sub>3</sub>, Na<sub>2</sub>O<sub>2</sub>. (O-atom)

Ans: (a) O.S. of S-atom in the given species is as :  $SO_3^{2-} = +4$ ,  $S_2O_4^{2-} = +3$ ,  $S_2O_6^{2-} = +5$ . Hence the increasing order is :

$$S_2O_4^{2-} < SO_3^{2-} < S_2O_6^{2-}$$
 (Ans)  
+3 +4 +5

(b) O.S. of O-atom in the given species is as :  $OF_2 = +2$ ,  $KO_2 = -1/2 = 0.5$ ,  $BaO_2 = -2/2 = -1$ ,  $O_3 = 0$ . Hence increasing order is :

(c) O.S. of O-atom in the given species is as :  $KO_3 = -1/3 = -0.33$ ,  $Na_2O_2 = -2/2 = -1$ . Hence increasing order is :

 $Na_2O_2 < KO_3$  (Ans) - 1 - 0.33

Q.7 Calculate the number of electrons transferred when one mole of  $KMnO_4$  is reduced to  $MnO_4^{2-}$ ,  $MnO_2$ ,  $Mn_2O_3$  and  $Mn^{2+}$ .

Ans : The reduction of one mole of  $KMnO_4$  or  $MnO_4^-$  to  $MnO_4^{2-},\ MnO_2$  ,  $Mn_2O_3$  and  $Mn^{2+}$  can be represented by the following reduction half-reactions.

#### **Oxidation-Reduction Reactions**

- (i)  $MnO_4^- + e^- \rightarrow MnO_4^{2-}$
- One mole
  - (ii)  $MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$ One mole
  - (*iii*)  $2MnO_4^- + 10H^+ + 8e^- \rightarrow Mn_2O_3 + 5H_2O_3$ Two moles
    - or  $MnO_4^- + 5H^+ + 4e^- \rightarrow \frac{1}{2} Mn_2O_3 + \frac{5}{2} H_2O$ one mole
  - (*iv*)  $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ one mole

Obviously the number of electrons transferred in the reduction of one mole of  $MnO_4^-$  to  $MnO_4^{2-}$ ,  $MnO_2$ ,  $Mn_2O_3$  and  $Mn^{2+}$  is 1, 3, 4 and 5 respectively.

Q.8 Find out the values of a, b, c and d in the following equation.

$$IO_3^- + a I^- + b H^+ \rightarrow c H_2O + d I_2$$

**Ans** : The given equation shows that  $IO_3^-(I = +5)$  is reduced to  $I_2(I = 0)$  and  $I^-(I = -1)$  is oxidised to  $I_2(I = 0)$ . Thus the given equatain can be broken into the following two balanced half-reactions :

$$\begin{array}{c} 2\mathrm{I}^{-} & \underbrace{\mathrm{Oxidation}}_{1_{2}} + 2e^{-}] \times 5 \\ \\ \underline{2\mathrm{IO}_{3}^{-} + 12\mathrm{\,H}^{+} + 10e^{-} & \underbrace{\mathrm{Reduction}}_{1_{2}} + 6\mathrm{H}_{2}\mathrm{O} \\ \\ \hline 10\mathrm{\,I}^{-} + 2\mathrm{\,IO}_{3}^{-} + 12\mathrm{\,H}^{+} & \longrightarrow 6\mathrm{\,I}_{2} + 6\mathrm{H}_{2}\mathrm{O} \end{array}$$

or

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 $5I^- + IO_3^- + 6H^+ \rightarrow 3I_2 + 3H_2O$ 

Thus the values of a, b, c and d are as : a = 5, b = 6, c = 3 and d = 3 (Ans)

## University Questions

1. Balance the following equations : (i)  $MnO_4^- + H^+ + H_2O \rightarrow Mn^{2+} + O_2 + H_2O$ (Calcutta 1997) (ii)  $\operatorname{Cr}_2\operatorname{O_7}^{2-} + \operatorname{H}_2\operatorname{SO}_3 \to \operatorname{Cr}^{3+} + \operatorname{HSO}_4^-$  (Acidic medium) (G. Nanakdev 2000) (iii) HCl + KMnO<sub>4</sub>  $\rightarrow$  Cl<sub>2</sub> + MnCl<sub>2</sub> + KCl + H<sub>2</sub>O (M.D. 2000) (iv)  $P_4 + HNO_3 \rightarrow H_3PO_4 + NO_2 + H_2O_4$ (G. Nanakdev 2000) 2. Determine oxidation number of : (i) Cr in  $Cr_2O_7^{2-}$  and  $CrO_4^{2-}$ (Garhwal 2000) (ii) S in Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> (G. Nanak Dev 2000) 3. Give points of distinction between valency and oxidation number. (M.D. 2000, Nagpur 2000) 4. Define oxidation and reduction in terms of oxidation number. (G. Nanakdev 2000) 5. Explain why  $H_2S$  is both an oxidant and reductant. (Himachal Pradesh 2000)

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- 6. What do you understand by the term "Oxidation Number"? Balance the following equation by oxidation number method. K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> + FeSO<sub>4</sub> + H<sub>2</sub>SO<sub>4</sub> → Cr<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> + H<sub>2</sub>O + Fe(SO<sub>4</sub>)<sub>3</sub> + K<sub>2</sub>SO<sub>4</sub> (Kumaon 2000)
  7. Name the oxy acids of chlorine with their formula. What is the oxidation number of chlorine in these acids ? [Gauhati (General) 2000]
  8. Give electronic interpretation of oxidation and reduction with suitable
  - examples. (Avadh 2000) • What is ovidation number? How is it determined? (M.D. Rohtak 2002)
- 9. What is oxidation number? How is it determined? (M.D. Rohtak 2002)
  10. Describe ion-electron method for balancing chemical equations.

(Lucknow 2002)

(Agra 2007)

**11.** O.N. of O-atom in O<sub>2</sub> molecule is : (a) 0 (b) -2 (c) +2 (d)  $-\frac{1}{2}$ 

**12.** Oxidation state of N in phosphazene is ... (H.N. Bahuguna 2007) **13.** In C + H<sub>2</sub>O  $\rightarrow$  CO + H<sub>2</sub>, H<sub>2</sub>O acts as :

- (a) Oxidising agent
- (b) Reducing agent
- (c) Oxidising and reducing agent both
- (d) None of these.
- 14. (a) Give the O.S. of Cr in  $CrO_5$ .

(b) Balance the equations :

- (i) Fe<sup>2+</sup> + Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> + H<sup>+</sup>  $\rightarrow$  ...
- (ii) Mn<sup>2+</sup> + PbO<sub>2</sub> + HSO<sub>4</sub><sup>-</sup>  $\rightarrow \dots$
- (iii) MnO<sub>4</sub><sup>-</sup> + Cr<sup>3+</sup> + H<sub>2</sub>O  $\rightarrow$  ...

15. The O.S. of Ni in Ni(CO)<sub>4</sub> is :

(a) 0 (b) 2 (c) 3 (d) 4

(H.N. Bahuguna 2007)

(Agra 2007)

(Agra 2007)