CHEMISTRY GE1 UNIT-2

IONIC BOND

This type of linkage is shown by two dissimilar atoms which form ions by the loss or gain of electrons. Atoms such as sodium, potassium, Magnesium etc. commonly lose valence electrons to form cations (Na^+, K^+, Mg^{2+}). Also atoms having valence shall containing six or seven electrons tend to take up electrons to complete this octet and form negative ions, i.e. anions (Cl^-, Br^-, O^{2-}).

Such eompounds which are formed by the transference of one or more electrons from one atom to the other are called electrovalent or ionic compounds and the type of linkage is called electrovalent linkage.

Example. *Formation of sodium chloride.*

In sodium chloride, we have

Sodium (At. no. Z = 11)	Chlorine (At No. Z = 17)
Electrons = 11	Electrons = 17
Protons = 11	Protons = 17

Electronic configuration : $1s^2\ 2s^2\ 2p^6\ 3s^1$

Electronic configutation : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$

There is only one electron in the valences shell of sodium atom and seven valence electrons in case of chlorine atom.

$$\mathrm{Na}^{\bullet} \xrightarrow{\text{Transfers valency electron}} \mathrm{:\ddot{C}l:}$$

$$\begin{array}{ccc} 2, 8, 1 & & 2, 8, 7 \\ \downarrow & & \downarrow \\ [\mathrm{Na}^+] & & [\mathrm{:Cl:}]^- \\ (2, 8) & & (2, 8, 8) \end{array}$$

Finally, the positive and the negatively charged ions get attracted by the electrostatic forces of attraction. $Na^+ Cl^- \rightarrow NaCl$. Ionic bond is strong as it is formed with a large decrease in energy.

The number of electrons lost or gained by an atom during the formation of ionic bond, is called **Electrovalency.** Thus, electrovalency of sodium is one and that of calcium is 2.

Nature of ionic bond

Ionic bond is non-directional in nature. A cation and an anion are considered as charged spheres. These ions have a uniform field of force around them. An ion can, therefore, attract ions having opposite charge from any direction (Fig. 2.1).

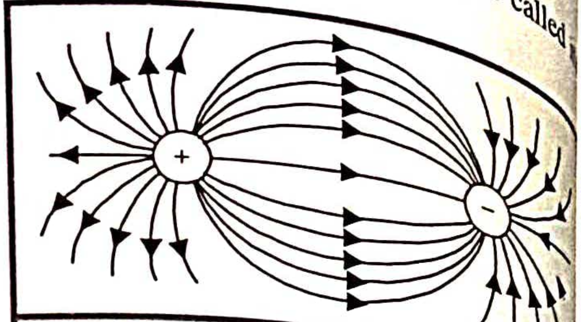


Fig. 2.1 Distribution of electrostatic field of two oppositely charged ions.

Hence an ionic bond is non-directional. The interaction between two oppositely charged ions, therefore, cannot fully compensate their electrostatic fields. Thus, each ion retains its power to attact ions of opposite charge from other directions. Hence each positive ion attracts as many negative ions at close distances as can be physically accommodated depending upon its size or radius. Similarly, each negative ion attracts positively charged ions from other directions. This results in a three dimensional aggregate of ions called **ionic crystal**. In an ionic crystal, the oppositely charged ions are arranged in a regular, continuous geometrical pattern. For example, in NaCl crystal, each sodium ion is surrounded by six equally spaced Cl^- ions and vice versa as shown in fig. 2.2. Geometry of the crystal is such that the force of attraction between oppositely charged ions is greater than the force of repulsion between similarly charged ions. This mutual attraction between oppositely charged ions holds them together in an ionic crystal and consitutes the ionic bond.

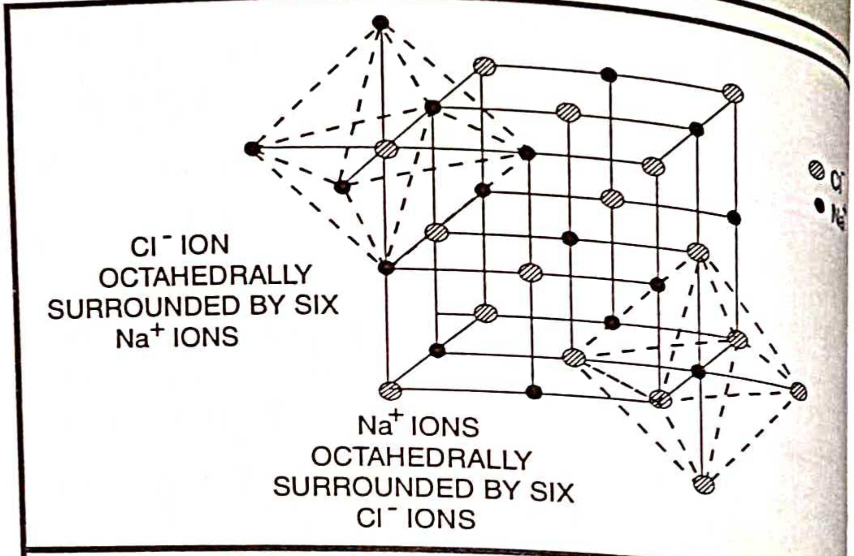


Fig. 2.2 Structure of NaCl.

Some examples of ionic bonds are shown in Fig. 2.3.

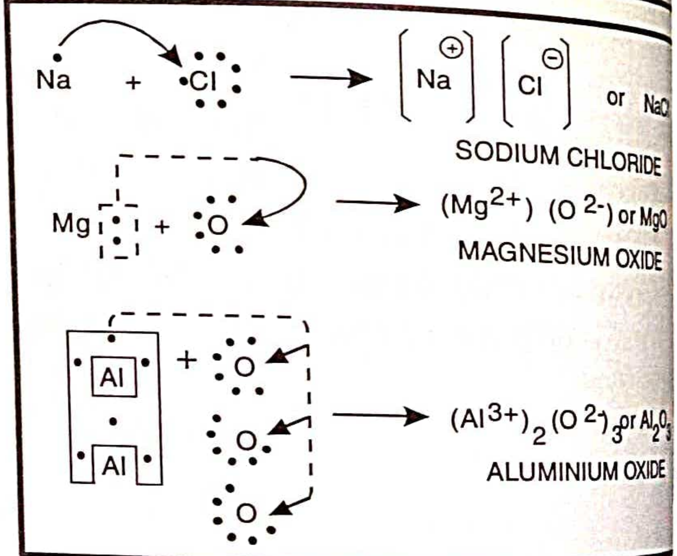


Fig. 2.3 Formation of some ionic compounds.

The formation of above compounds is explained below :

(*i*) **In NaCl** molecule, one valence electron from Na-atom is transferred to Cl-atom. Thus, Na and Cl-atoms attain stable neon and argon gas configuration respectively.

(*ii*) **In MgO,** two valence electrons from Mg atom are transferred to O-atom. Thus Mg and O-atom attain stable neon gas configuration.

(*iii*) **In Al_2O_3,** six valence electrons on two Al-Atoms are transferred equally to three oxygen atoms. Thus, all aluminium and oxygen atoms attain stable neon gas configuration.

Factors influencing the formation of ionic bond. Following are the factors which favour the formation and stability of ionic bonds.

(*a*) **Low Ionisation energy.** Ionisation energy of an element is the amount of energy required to remove an electron from the outermost shell of an Isolated neutral gaseous atom to form gaseous cation.

Lesser the ionisation energy, easier is the removal of an electron. Ionisation energy of alkali metals (Na, K etc.) is low and thus, they have more tendency to form positive ions. The ionisation energy of alkaline earth metals (Mg, Ca etc.) is higher and they form cations not so easily. For example, ionisation energy of sodium is 495 kJ mol^{-1} while that of Magnesium is 743 kJ mol^{-1}.

$$Na_{(g)} \xrightarrow{495\ kJ\ mol^{-1}} Na^+_{(g)} + e \ ; \qquad Mg_{(g)} \xrightarrow{743\ kJ\ mol^{-1}} Mg^+_{(g)} + e$$

The energy required to remove second electron is very high and thus, the formation of Mg^{2+} ion is relatively difficult. In case of Aluminium, the formation of Al^{3+} ion requires 3158 kJ mol^{-1}. This much energy is generally not available and hence Aluminium does not form ionic bond. For Ionic bond formation, the Ionisation energy of the metal should be low.

(*b*) **High Electron affinity.** It is defined as the amount of energy released when an extra electron is added to an Isolated gaseous atom to form gaseous anion. Higher the electron affinity, more is the quantity of energy released and easier is the formation of ionic bond. The electron affinity of chlorine is the highest in the periodic table. It is 348 kJ mol^{-1}. Group 16 elements (oxygen, sulphur etc.) do form divalent anions and in this case, the formation of divalent anion from monovalent anion requires energy. Thus group 16 elements form ionic bonds with lesser ease compared to group 17 elements. **For ionic bond formation, the electron affinity of an element should be high.**

(*c*) **Higher Lattice energy.** For ionic bond formation, the oppositely charged ions combine with the large decrease in energy.

The energy released when the oppositely charged ions combine to form one mole of the ionic compound is called Lattice energy.

The higher the value of lattice energy of the ionic compound, the greater is the stability of the compound and also easier is its formation.

The force of attraction between the oppositely charged ions is directly proportional to the magnitude of charges and varies inversely to the square of the distance between them.

$$\text{Force of attraction} = \frac{q_1 q_2}{D^2}$$

Hence, the value of lattice energy of an ionic compound depends upon the following factors.

(*i*) **Charge on the ions.** The higher the magnitude of charge on the ions, greater is the force of attraction and higher is the lattice energy.

(*ii*) **Size of the ions.** Smaller the sizes of the ions, lesser will be the internuclear distance and greater is the force of attraction.

Characteristics of Ionic compounds

The important characteristics of ionic compounds are as follows :

1. Hard and rigid. The ionic solids are hard and rigid, because the oppositely charged ions are tightly bound together by strong attractive forces.

2. High density. The electrostatic strong attraction between the cations and anions in an ionic compound bring them very close to one another. This decreases the volume of the system and its density increases.

3. High melting and boiling points. Ionic compounds have high melting points because the oppositely charged ions have a very strong electrostatic force of attraction between them. A large amount of energy in the form of heat is needed to overcome this force and cause fusion or vapourisation of ionic compound.

4. Electrical conductivity. Ionic compounds conduct electricity in the fused state or in aqueous solution. In the fused state or in solution, the cations and anions are mobile and on passing electric current through the electrolyte, they migrate to opposite electrodes.

5. Crystal structure. Ionic compounds do not exist as individual neutral molecules. The ionic bonds are non-directional. Thus, in order to occupy the minimum space, the ions in an ionic solid arrange themselves in a regular geometrical order, which is called a crystal or lattice. In a crystal of sodium chloride (Fig. 2.4). each Na^+ ion is surrounded by six Cl^- ions and each chloride ion is surrounded by six Na^+ ions forming a cubic crystal lattice.

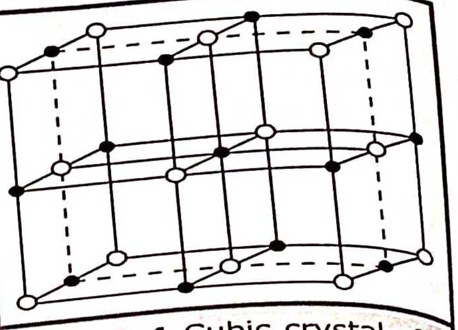


Fig. 2.4 Cubic crystal of NaCl.

6. Solubility in water. Ionic compounds are usually soluble in polar solvents like water which have high values of dielectric constant. In solution, the ions are free to move and interact with solvent molecules.

ENERGY CONSIDERATION IN IONIC BONDING

(*a*) **Lattice Energy.** It is known that the elements combine to form a compound only if the overall process results in the lowering of energy. When the elements combine to form one mole of the compound, then the net-amount of energy released is calculated. More the energy released, stronger is the bond.

Lattice energy of a compound is defined as the amount of energy released when one mole of the compound is formed due to electrostatic attraction between oppositely charged ions.

The energy changes involved in the formation of ionic compounds from their constituent elements can be studied with the help of thermochemical cycle, called Born-Haber Cycle.

Higher lattice energy means greater stability of ionic compound and greater attraction between the cations and anions. Hence, compounds having higher lattice energy have higher magnitude of the properties such as melting points and boiling points.

It may be noted that the stability of an ionic bond mainly depends upon the magnitude of lattice energy which itself depends upon the following factors :

(*a*) **Size of ions.** If the size of ions is small, the inter-ionic attraction increases and the energy of th system decreases. This adds to the strength and stability of ionic bond *e.g.*, the ionic radius of Na^+-io (0.95 Å) is smaller than that of K^+-ion 1.33 Å). As a result, the force of attraction between Na^+ and Cl^- ion will be more than that between K^+ and Cl^- ions. Thus, NaCl bond is stronger than KCl bond.

Hence, *strength and stability of ionic bond* $\propto \dfrac{1}{\text{size of ion}}$.

(*b*) **Charge on ions.** Inter-ionic attraction increases with increase in charge on ions. Hence energy the system decreases. This adds to the strength and stability of ionic bond. Thus, *strength and stability ionic bond is directly proportional to the charge on ions.*

Ionic bond formation involves decrease in energy. The total heat change in the formation of 1 mole of crystalline NaCl from Na (*s*) and $Cl_2(g)$ is

$= (108.5 + 121.5 + 496 - 394 - 760)\ \text{kJ} = -428\ \text{kJ}.$

Therefore, 428 kJ of heat is liberated in the formation of 1 mole of crystalline sodium chloride. Hence NaCl is stable as compared to Na(*s*) and $Cl_2(g)$.

Statement of Born-Lande equation and Calculation of Lattice Energies (U_0) of Ionic Solids

Derivation of Born-Lande Equation: The lattice energy of an ionic crystal is determined by coulombic interactions between all of its ions present in the crystal. These interactions are of two types.

(*i*) Attractive interactions between ions of opposite charge.

(*ii*) Repulsive interactions due to interpenetration of similarly charged electron charge clouds.

I. Attractive interactions between ions of opposite charge. Consider a pair of ions of opposite charges Z_1 and Z_2. Let e be the electronic charge. If *r* is the distance between the ions then potential energy of a pair of ions is given by the relation.

$$\text{P.E. (attraction)} = Z_1 Z_2 \frac{(+e)(-e)}{r} = -\frac{Z_1 Z_2 e^2}{r} \qquad \text{...(1)}$$

In case of $Na^{+1}\ Cl^{-1}$, $Z_1 = 1$, $Z_2 = 1$

In case of $Ca^{+2}\ F_2^-$, $Z_1 = 2$, $Z_2 = 1$.

II. Repulsive interaction due to interpenetration of similarly charged electron charge cloud. When a cation comes very close to an anion, interpenetration of similarly charged electron charge cloud takes place and repulsion results between them. The potential energy due to this repulsion is inversely proportional to the *n*th power of the distance between the ions. Thus,

$$\text{P.E}_{(\text{repulsion})} = \frac{be^2}{r^n}$$

where *b* is repulsion co-efficient and *n* is Born exponent. ...(2)

For ions having neon configuration (*e.g.*, $_{11}Na^+$, $_9F^-$, $n = 7$).

For ions having $_{18}Ar$, $_{36}Kr$ and $_{54}Xe$ configurations, $n = 9$, 10 and 12 respectively.

∴ The net potential energy for a pair of ions of opposite charge obtained by combining equations (1) and (2)

$$= -\frac{Z_1 Z_2 e^2}{r} + \frac{be^2}{r^n} \qquad \text{...(3)}$$

This equation (3) is called **Born equation.**

This equation gives the energy released when a cation separated from an anion in gaseous state by an infinite distance is brought at a distance *r* in a crystal. The equation also indicates that $\frac{be^2}{r^n}$ repulsion term increases more rapidly than first term with decrease in the magnitude of *r*.

Application of Born equation

Born equation is useful to calculate the lattice energies of ionic crystals. For example, let us consider the forces of attraction and repulsion involved in a crystal of sodium chloride. In a crystal, there are a large number of cations and anions and not one cation and one anion only. These ions are arranged together in a specific geometry. Thus, we are to consider the forces of attraction and repulsion between all the ions. In case of sodium chloride crystal, **each Na^+ ion is surrounded by**

(*i*) 6 Cl^- ions at a distance, r

(*ii*) 8 more Cl^- ions at a distance, $\sqrt{3}\,r$

(*iii*) 24 more Cl^- ions at a distance, $\sqrt{5}\,r$

(*iv*) 6 more Na^+ ions at a distance, $2r$

(*v*) 12 more Na^+ ions at a distance, $\sqrt{2}\,r$

(*vi*) 24 more Na^+ ions at a distance, $\sqrt{6}\,r$ and so on.

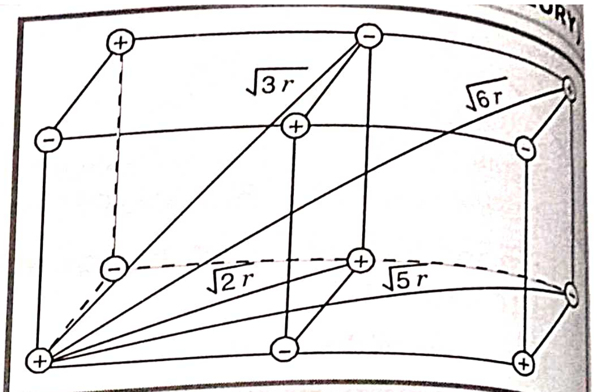


Fig. 2.5 Inter-ionic distances in NaCl crystal.

Because of above arrangement, there will be forces of attraction between Na^+ and Cl^- ions and forces of repulsion between Na^+ and Na^+ ions. Forces of attraction lead to lowering of energy and hence potential energy is given a negative sign. Forces of repulsion lead to rise in potential energy and hence potential energy is given a positive sign. By adding the effect of all the above attraction and repulsion interactions, the **first term** in the Born equation (3) can be calculated. Thus,

$$(\text{P.E})_1 = -\frac{6Z_1Z_2e^2}{r} - \frac{8Z_1Z_2e^2}{\sqrt{3}\,r} - \frac{24Z_1Z_2e^2}{\sqrt{5}\,r} + \frac{6Z_1Z_2e^2}{2r} + \frac{12Z_1Z_2e^2}{\sqrt{2}\,r} + \frac{24Z_1Z_2e^2}{\sqrt{6}\,r} + \ldots.$$

$$= -\frac{Z_1Z_2e^2}{r}\left[6 - \frac{8}{\sqrt{3}} - \frac{24}{\sqrt{5}} + \frac{6}{2} + \frac{12}{\sqrt{2}} + \frac{24}{\sqrt{6}} + \ldots.\right]$$

$Na^{+1}\,Cl^{-1}$ is a uni-univalent ion. So, for NaCl.$Z_1 = 1$, $Z_2 = 1$. The sum total of all the terms in the brackets gives rise to a quantity called Madelung constant (symbol, A) for sodium chloride. The *Value of A for NaCl is 1.747558*. All the salts having geometrical arrangement similar to NaCl, will have same value of A. The value of A for all salts can be calculated provided, the geometrical arrangements of the ions in their crystals is known.

Thus, the first term in Born equation can be written as :

$$(\text{P.E})_1 = \frac{AZ_1Z_2e^2}{r} \qquad \ldots(4)$$

$$= \frac{AZ^2\,e^2}{r} \;[\text{when } Z_1 = Z_2 = Z] \qquad \ldots(5)$$

Madelung constants for some salts whose crystal structures are known are given in Table 2.1 while values of Born exponents for different ion types are given in table 2.2.

Let us consider the second term in Born equation (3). This term arises because as a cation and an anion come very close to each other, there is a repulsion between them because of interpenetration of similarly charged electron charge cloud. This term varies inversely as nth power of r. So, it is useful to consider only the *nearest neighbours and not farthest ions*. In **sodium chloride crystal**, each Na^+ ion is surrounded by six Cl^--ions. So, repulsion energy term $= \dfrac{6\,be^2}{r^n}$.

The term $6\,be^2$ is generally replaced by the term B where

$B = be^2 \times$ number of nearest neighbours.

$$\therefore \textbf{ Second term } = \frac{B}{r^n} \qquad \text{...(6)}$$

Taking into consideration, the forces due to all the neighbouring ions, the potential energy of an ion in a crystal can be given by the relation

$$\text{P.E .} = \frac{AZ^2e^2}{r} + \frac{B}{r^n} \qquad \text{...(7)}$$

The value of n varies from 7 to 12 for a large number of common ions.

For an easy solution of equation (7), the factor B should be eliminated. It can be done by realising that an ion will be in stable equilibrium position when attractive and repulsive forces acting on it are equally balanced. In this situation, the potential energy of the ion is minimum and $d(\text{P.E})/dr =$ zero. Also, interionic distance, r may be taken as r_0.

Thus, constant B can be eliminated by differentiating equation (3) with respect to r and equating it to zero.

$$\therefore \qquad \text{P.E.} = -AZ^2e^2r^{-1} + Br^{-n} \quad \text{...(c.f. equation, 7)}$$

$$\frac{d}{dr}(\text{P.E}) = -AZ^2e^2(-1)\,r^{-2} + B(-n)\,r^{(-n-1)} \qquad \left[\because \frac{d}{dx}x^n = nx^{n-1}\right]$$

$$= AZ^2e^2r^{-2} - nB\,r^{(-n-1)}$$

Since $\dfrac{d}{dr}(\text{P.E}) = 0$ and $r = r_0$,

we have $AZ^2e^2r_0^{-2} - nB\,r_0^{(-n-1)} = 0$ or $AZ^2e^2r_0^{-2} = nB\,r_0^{(-n-1)}$

$$\therefore \qquad \frac{r_0^{-2}}{r_0^{(-n-1)}} = \frac{nB}{AZ^2e^2}\,; \qquad r_0^{n-1} = \frac{nB}{AZ^2e^2}$$

$$r_0 = \left(\frac{nB}{AZ^2e^2}\right)^{\frac{1}{n-1}} \text{ and } B = \frac{AZ^2r_0^{n-1}e^2}{n} \qquad \text{...(8)}$$

Substituting the value of B from equation (8) in equation (7), we get

$$(\text{P.E})_0 = -\frac{AZ^2e^2}{r_0} + \frac{AZ^2e^2}{nr_0^n}r_0^{n-1} = -\frac{AZ^2e^2}{r_0} + \frac{AZ^2e^2}{nr_0} = \frac{AZ^2e^2}{r_0}\left(\frac{1}{n} - 1\right) \qquad \text{...(9)}$$

Since **lattice energy,** U_0 is defined as the amount of energy released when one mole of a crystal is formed from the constituent gaseous ions separated at infinite distance from one another, hence

$$U_0 = N_0 \times P.E \qquad ...(10)$$

where N_0 = Avogadro's number and P.E. = Potential energy.

Substituting the value of P.E. from (9) in (10), we get

$$U_0 = \frac{N_0 \, AZ^2 e^2}{r_0}\left(\frac{1}{n} - 1\right) \qquad ...(11)$$

This equation is called **Born-Lande equation.**

Since n is always greater than 1, hence U_0 will always be negative as expected.

The equation (11) is useful to calculate the lattice energy of a given crystal provided the value of n can be calculated from the compressibility of the given crystal and the crystal spacing parameters are known. The validity of equation (11) can be easily seen by comparing the lattice energies obtained from equation (11) and experimental values (Table 2.3).

BORN-HABER CYCLE

It has been observed that lattice energy of a very few compounds has been determined directly. However, a cyclic process called **Born Haber cycle** has been devised. It is helpful to calculate lattice energy in terms of thermo-chemical quantities like ionisation energy, electron affinity, etc. The formation of ionic solid can be described by two processes.

1. Direct process. M(s) and $\frac{1}{2}X_2$ (g) combine directly in one step reaction and energy is released which is equal to the heat of formation of MX.

$$M(s) + \frac{1}{2}X_2(g) \xrightarrow{\text{direct combination}} MX\ (\text{solid}) \qquad (\Delta H_{form})_{MX} = -\ ve$$

2. Alternative process (a) Sublimation of M(s) to M(g). Here one mole of solid M absorbs energy equal to its sublimation energy, $(\Delta H_{sub})_M$ and is converted to gaseous M(g).

$$M(s) + (\Delta H_{sub})_M \xrightarrow{\text{Sublimation}} M\ (g)$$

where ΔH represents difference in enthalpy (heat content) between initial state M(s) and final state M(g).

(*b*) **Dissociation.** In this step, $\frac{1}{2}$ mole of X_2 absorbs energy equal to half the dissociation energy of $X_2(g)$, *i.e.*, $\frac{1}{2}$ $(\Delta H_{diss})_{X_2}$ and is converted to X(g).

$$\frac{1}{2}X_2\ (g)\ \frac{1}{2}(\Delta H_{diss})_{X_2} \xrightarrow{\text{Dissociation}} X(g)$$

(*c*) **Ionisation of M(g) to M^+ (g).** M(g) atom absorbs energy equal to ionisation energy, (1E) M and is converted to M^+ (g) ion.

$$M(g) + (IP)_M \xrightarrow{\text{Ionisation}} M^+(g) + e^-$$

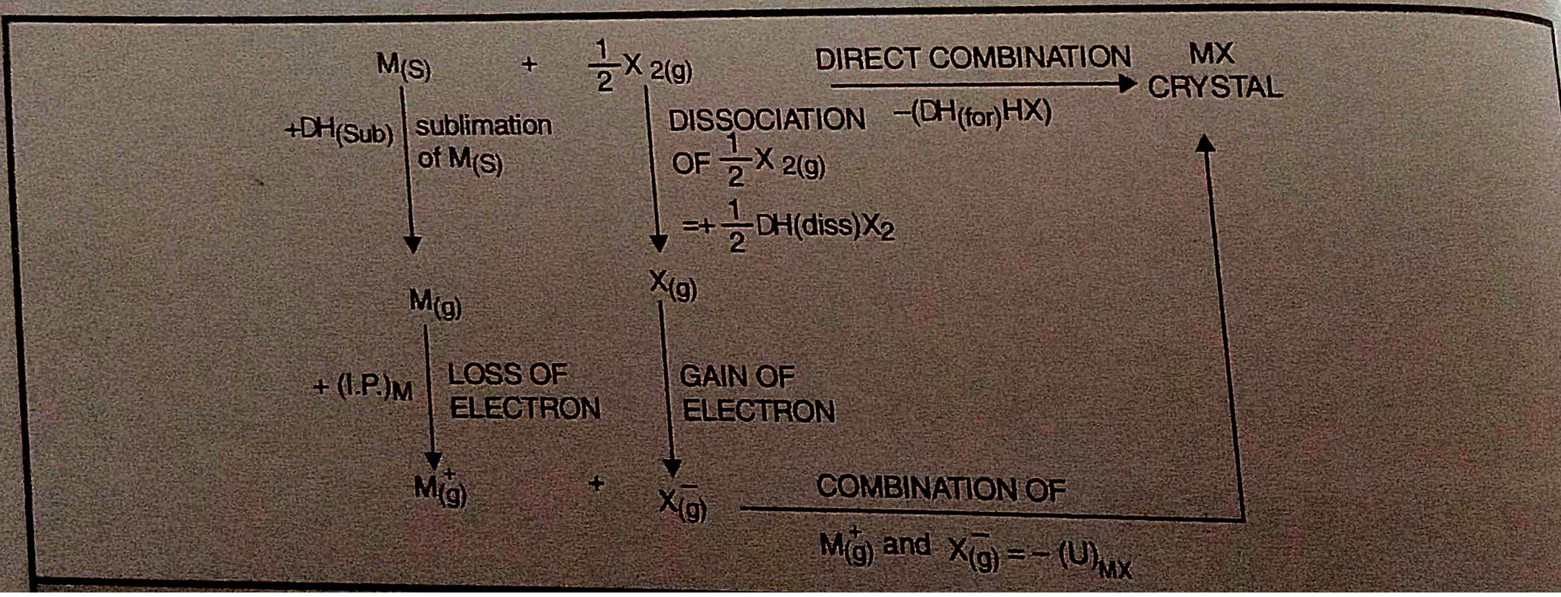
(*d*) **Conversion of X(g) to X^- (g).** X (g) atom takes up the electron given out by M (g) to form X^- (g). In this step, energy released is equal to its electron affinity, $(EA)_X$.

$$X(g) + e^- \xrightarrow[\text{electrons}]{\text{gain off}} X^-(g) + (EA)_g$$

(*e*) **Combination of M^+ (g) and X^- (g) to form MX.** In this step M^+ (*g*) combines with X^-(*g*) to form one mole of MX (solid). Hence, energy equal to the lattice energy of MX, $(U)_{MX}$ is released.

$$M^+ (g) + X^- (g) \xrightarrow{\text{Combination}} MX \text{ (crystal)} + (U)_{MX}$$

The whole process can be diagrammatically represented below (Fig. 2.6).



APPLICATIONS OF BORN HABER CYCLE

Born Haber Cycle is very useful to calculate many properties as described below.

1. Calculation of electron affinities (EA). It is used to calculate the electron affinities of elements which are difficult to measure by other methods. The heat of formation (ΔH_f) of a compound is given by the following relation

$$\Delta H_f = S + \frac{1}{2} D + IE + EA + U_0$$

$$\therefore \quad E.A. = \Delta H_f - S - \frac{1}{2} D - IE - U_0$$

Where ΔH_f = heat of formation ; S = heat of sublimation ; D = dissociation energy ; EA = Electron affinity ; I.E. = Ionisation energy ; and U_0 = lattice energy. In the above case, U_0 can be calculated with the help of Born Lande equation while ΔH_f, S, D, IE can be determined experimentally.

EXAMPLE 5. Find the electron affinity (EA) of iodine with the help of following data (in kcal mol^{-1}) ΔH_f (NaI) = − 68.8

$U_{NaI} = -165.4$; $\Delta H_{(s)}$ (Na) = 25.9 ; ΔH_{diss} (I_2) = 51.0 ; $IE_{(Na)}$ = 118.4.

SOLUTION. We know that

$$\Delta H_f (NaI) = \Delta H_{(s)}(Na) + \frac{1}{2} \Delta H_{diss} I_2 + IE_{Na} + EA_{(I)} + U_{NaI}$$

Substituting the values, we get

$$-68.8 = 25.9 + \frac{1}{2} \times 51 + 118.4 + EA_{(I)} - 165.4$$

$$\therefore \quad EA_{(I)} = 165.4 - 68.8 - 25.9 - 25.5 - 118.4 = \mathbf{-73.2\ kcal\ mol^{-1}}.$$

2. Estimation of proton affinities (PA). This cycle is used to determine the proton affinities of different bases. The proton affinity of a base X is the amount of energy released in the reaction:

$$X(g) + H^+(g) \longrightarrow XH^+ (g)$$

For example, the proton affinity (PA) of ammonia can be expressed as follows :

$$NH_3 (g) + H^+ \longrightarrow NH_4^+ (g) ; \Delta H = PA$$

Following equation can be used to calculate the proton affinity of ammonia.

$$\Delta H_f = \Delta H_{diss} + IE + EA + PA + U_0 \qquad ...(1)$$

Where ΔH_f = enthalpy of formation of NH_4^+ ;

ΔH_{diss} = heat of dissociation ; IE = ionisation energy ;

EA = electron affinity ; PA = proton affinity and

U_0 = lattice energy which can be calculated with the help of Born Lande equation.

For the reaction $NH_3 (g) + HCl (g) \longrightarrow NH_4^+ Cl^- (s)$

$\Delta H_f = -144.5$ kJ mol^- ; $U_0 = -648.5$ kJ mol^- ; IE = 1311.6 kJ mol^-

EA = − 347.2 kJ mol^- and ΔH_{diss} = 430.9 KJ

Substituting these values in equation (1) we get

$$-144.5 = 430.9 + 1311.6 - 347.2 + PA - 648.5$$

$$\therefore \quad PA = -891.3\ kJ$$

Since proton affinity of ammonia is negative, the reaction is favourable. Hence ammonia has a good tendency to accept a proton.

3. Stability of ionic compounds. This cycle helps to understand the stabilities of many ionic compounds. For example, it explains why MgO is a stable compound. When the values of ΔH_{diss}, I.E., E.A., ΔH_{sub} and lattice energy (U_0) is substituted in the following equation

$$\Delta H_f = \Delta H_{sub} + \frac{1}{2}\,\Delta H_{diss} + IE + EA + U_0$$

We get high negative value of ΔH_f (MgO) which indicates that MgO is stable.

4. Formation of ionic compounds in higher oxidation states. This cycle helps to understand why some metals are unable to form stable compounds in their low oxidation state. For example, $CaCl_2$ is a stable compound while CaCl is not formed although the energy needed to form Ca^+ (*g*) and Cl^- (*g*) ions is lower than that needed for the formation of Ca^{2+} (*g*) and Cl^- (*g*) from Ca(s) and $Cl_2(g)$. In such cases, the value of ΔH_f ($CaCl_2$) calculated from the equation

$$\Delta H_f = \Delta H_{sub} + \frac{1}{2}\,\Delta H_{diss} + IE + EA + U_0 \quad \text{is negative.}$$

So, $CaCl_2$ is formed.

On the same basis we can prove that $NaCl_2$ is not formed because by using Born Haber Cycle, the value of ΔH_f comes out to be positive.

5. To predict the feasibility of a reaction. Born Haber Cycle can be used to calculate the heat of formation (ΔH_f) of an unknown compound. If ΔH_f comes out to be positive, the reaction is energetically unfavourable. If ΔH_f is negative, the compound is formed.

Strength of ionic bond. Greater the energy required to separate a pair of ions, greater is the strength of ionic bond. It has been observed that :

The energy required to separate a pair of ions is approximately proportional to $\dfrac{Z_1Z_2}{r^+ + r^-}$ where

(*i*) Z_1 and Z_2 are the charges on cation and anion respectively, and

(*ii*) r^+ and r^- are the radii of cation and anion respectively.

Thus, the hardness (table 2.4) and melting point (table 1.6) of the crystals having similar charged ions must vary inversely as inter-ionic distance ($r^+ + r^-$).

Signature of Invigilator

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Marks Secured	Full Mark	Signature of Examiner
+3 8e IInd (Major Elective) Paper I		

WRITING SPACE

Solvation energy - (Dissolution of Electrolytes)
(Ionic compound).

The different compounds dissolves to different extent in solvent due to followings factors:-

1) Dielectric constant:-

According to coulomb's law of electrostatic force of attraction
$$F = \frac{q_1 q_2}{D r^2} \quad ①$$
$$q_1 \xleftrightarrow[\;r\;]{} q_2$$

where D = Dielectric constant of solvent.

Greater will be the value of 'D', Smaller will be the value of F and greater will be the solubility in the solvent

Ex NaCl is more soluble in water (D = 80) than ethyl alcohol (D = 25)

ⅱ Lattice energy:-

The lattice energy of an ionic compound is inversely proportional to its tendency to dissolve.

Thus. Smaller the lattice energy, greater is the tendency of an ionic solid to dissolve.

Ex Na_2SO_4 + water = Highly soluble

But $PbSO_4$ + water = slightly soluble.

This ~~[illegible]~~ is because the lattice energy of $PbSO_4$ is greater than Na_2SO_4.

ⅲ Solvation of ions:-

When an ionic solid is added to a solvent, the cations and anions present in this solid get respectively surrounded by the negative and Positive ends of the solvent molecules, partly neutralise the charge of the ions and also act as an insulating sphere.

Dielectric effect:- The insulating effect is known as dielectric effect.

Solvation:- The ion-dipole interaction which results in loose combination between the ions and solvent molecules is called solvation.

If the solvent is water it is called Hydration.

Solvation energy:- The energy released during solvation or hydration is known as solvation energy or hydration energy.

Ex $K^+_{(g)}$ + water ⟶ $K^+_{(aq)}$ + Hydration energy
One mole (one mole of hydrated ion)

Greater the hydration energy, greater in the solubility of the ionic solid.

Imp
Ions with small size and high charge gets heavily hydrated and have maximum hydration energy.
Imp

Born-Haber cycle

The lattice energy of a very few compounds has been determined directly. However a cyclic process called Born-Haber cycle has been devised.
The formation ~~of formation~~ of ionic solid can be described by the two process.

① **Direct process**:- When $M_{(s)}$ and $\frac{1}{2}X_{2(g)}$ combine directly in one step by an arrow (⟶)

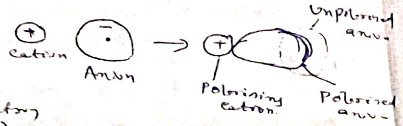
$\overset{+\longrightarrow}{H \longrightarrow Cl}$ (μ = 1.92D)

Fajan's rule or theory :- The rule deals with the covalent character in ionic bonds. As we know, due to difference in electronegativity in bonded atoms, polar character arises in a covalent bond. It have been observed that some covalent character is also present in an ionic bond

Ex LiCl Li = 0.1 and Cl = 3.0 (Electronegativity)

Electronegativity difference $\boxed{2.9}$. So LiCl is expected to be purely ionic compound. But its solubility in organic solvent indicates that it possesses covalent character too. Such behaviour of ionic compound is explained by Fajan's rule or theory

Consider a cation (A+) and an anion (B⁻)



As these ~~are~~ come closer to the cation attracts the electron cloud of anion and repels its nucleus

Thus the anion get distorted and its electron cloud is tilted towards the cation.

In this way, the sharing of electrons occur between two nuclei

The power of an ion to distort the electron cloud of ~~anion~~ another ion is called its polarising power.

On the other hand :-

The tendency of anion to get polarised by the other ion is called its polarizability.

As the size of anion is greater than cation and its electron less tightly bonded to the nucleus. So it possesses high polarizability.

Imp Greater the distortion or polarizability, greater is the covalent character in that ionic bond. ✓

Fajan's rule deal with the factor which favour the polarization of ion. These are.

ⓐ High charge :- Higher the charge on a cation greater will be its polarizing power.

Ex $Mg^{2+} > Li^{+}$

Higher the charge ~~of~~ on anion, higher will be its polarizability. Ex ($O^{2-} > F^{-}$)

Hence high charge on ions favour more polarization.

ⓑ ~~low~~ Small size of cation :- The smaller the size of cation, greater will be its force of attraction for the electron of anion. Hence greater will be its polarizing power. Ex Polarising power of $Li^{+} > Na^{+}$.

ⓒ ~~Small size~~ large size of anion :- The larger the size of anion less tightly its electron will be held. Hence these are largely polarized

Ex I^{-} is largely ~~Polari~~ polarized than Cl^{-}!

Dipole Moment and Percentage Ionic character.

The concept of dipolemoment is helpful to find the percentage of ionic character in a molecule

This is explained as:-

$$\text{Percentage of ionic character} = \frac{\text{Experimental D.M}}{\text{Theoretical D.M}} \times 100$$

Ex Method to find percentage ionic character in HCl (using C.G.S Unit). Let the bond between H and Cl atoms in HCl be completely ionic

(i) charge on H^{+} and Cl^{-} ion = 1.6×10^{-10} coulomb.
= 4.8×10^{-10} e.s.u

(ii) In HCl bond length = 1.27A° = 1.27×10^{-8} cm (1A° = 10^{-8} cm)

∴ Dipolemoment of HCl = charge × distance
= 4.8×10^{-10} e.s.u $\times 1.27 \times 10^{-8}$ cm
= 6.1 ~~× esu~~ 10^{-18} e.s.u cm
= 6.1 D (theoretical) (1D = 10^{-18} esu cm)

Dipolemoment of HCl = 1.03 D (By experimentally)

∴ %age of ionic character of HCl = $\frac{\text{Expt D.M}}{\text{Theo D.M}} \times 100 = \frac{1.03}{6.1} \times 100$
= 16.9

1. Geometry of the molecules with central atom having lone pairs of electrons (Irregular geometry). A molecule will have irregular geometry if the repulsive interactions between the electron pairs (around the central atom) are not of equal magnitude.

Conditions for irregular geometry. A molecule will have irregular geometry if it satisfies any one of the following conditions :

(*i*) The central atom of the molecule should not be bonded to all the similar atoms, *e.g.*, $CHCl_3$, $CHBr_3$.

(*ii*) The central atom should have one or more lone pair of electrons in addition to one or more bond pair of electrons *e.g.*, $\ddot{N}H_3$ and $H_2\ddot{\underset{\cdot\cdot}{O}}$.

The presence of lone pairs on the central atom causes lone pair-lone-pair and lone pair– bond-pair repulsive interactions in addition to the bond pair–bond pair repulsive interactions. The additional repulsive interactions distort the regular geometry of the molecule. Being surrounded by bonding as well as lone pairs of electrons, the shape is tetrahedral but the bond angles are no longer 109° 28′. Let us now consider the molecules of this type.

(*a*) **Shape of NH_3 molecule. Pyramidal.** In NH_3, the central atom is $_7N$. It has the configuration $1s^2 2s^2 2p_x^1\ 2p_y^1\ 2p_z^1$ in the ground state. It can make three bonds with three hydrogen atoms due to the presence of three unpaired electrons in it. In the formation of NH_3, each of these electrons is shared by three hydrogen atoms. As a result, the nitrogen atom is surrounded by three shared pairs of electrons. One lone pair of electrons still remains in the valence shell of nitrogen atom (Fig. 2.11).

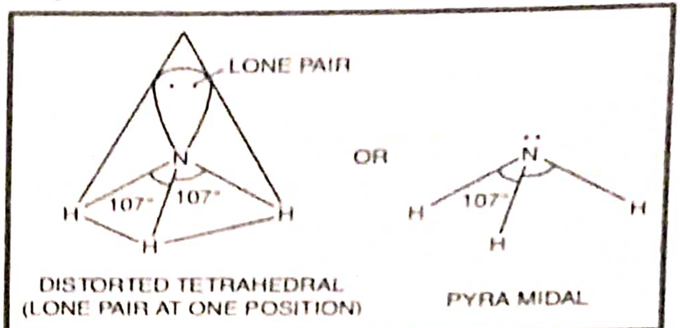


Fig. 2.11 Distorted tetrahedral or pyramidal shape of Ammonia.

Total number of electrons in the valence shell of nitrogen = 5

Bonds made by nitrogen = 3

Shared pairs of electrons around Nitrogen = 3

Unshared pairs of electrons around Nitrogen $= \frac{1}{2}(5 - 3) = 1$

Total number of stereoactive pairs around nitrogen = 3 + 1 = 4

As the central nitrogen atom is surrounded by shared as well as unshared pairs of electrons, therefore, the force of repulsion among electron pairs is unequal. Hence, NH_3 molecule has an irregular or **distorted tetrahedral** geometry. It is also known as **pyramidal** geometry. In such a geometry, the central atom (N) lies at the centre of a tetrahedron. The three N – H bonds are directed towards the three corners of this tetrahedron while the fourth corner is occupied by a lone pair. Each H – N – H bond angle is 107°.

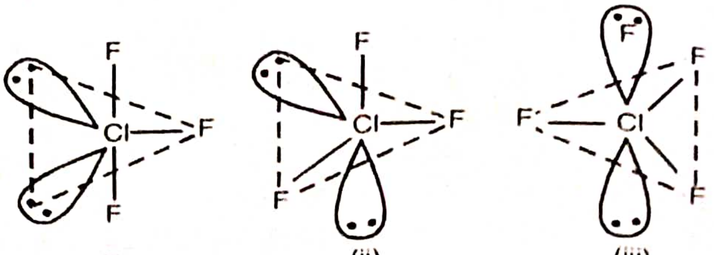
Explanation for decrease in bond angles. The H – N – H bond angle in NH_3 (107°) is less than the normal tetrahedral value (109° – 28′). This is because the lone pair-bond pair repulsion is greater than bond pair-bond pair repulsion. As a result, the bond pairs move away from the lone pair (to decrease repulsion) and come closer to each other. Hence, angle between bond pairs decreases.

2. Shape of ClF_3 (Chlorine trifluoride). $_{17}Cl = (Ne)^{10}\ 3s^2$; $_9F = (He)^2\ 2s^2 2p^5$. So, valence electrons in Cl and F atoms are 7 (2 of 3*s* and 5 of 3*p*) and 7 (2 of 2*s* and 5 of 2*p*) respectively. Hence total number of valence electrons in $ClF_3 = 7 + (3 \times 7) = 28$. After putting in single bonds and distributing two lone pairs, the Lewis structure of ClF_3 is shown. Here number of Cl – F single bonds (*bp*) = 3 and lone pair of electrons (*lp*) = 2 [∵ lone pairs = 1/2 (valence electrons of Cl atom minus bonds made by Cl) = (7 – 3)/2 = 2].

So, stereoactive electron pairs around Cl-atom = number of bonds plus number of lone pairs = 3 + 2 = 5.

Since Cl atom is ClF_3 is surrounded by three electron pairs (*bp*) and two lone pairs (*lp*), the lone pair repulsion among electron pairs is not equal (*lp-lp* repulsion > *lp-bp* repulsion > *bp* – *bp* repulsion).

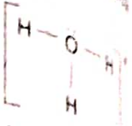
The molecular has five electron pairs and it should have trigonal bipyramidal geometry in which t positions are occupied by lone pairs. Thus, the molecule can have the following probable steuctures



(i) (ii) (iii)

Structure (*i*) appears to be most stable as it will experience lesser repulsion in comparison to structures (*ii*) and (*iii*). Clearly, the molecule has **T-shaped** structure and bond angle is 87.6°.

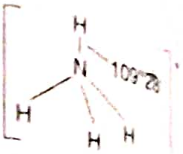
3. H_3O^+ (Hydronium ion). $_8O = 1s^2\ 2s^2\ 2p^4$; $_1H = 1s^1$. Total number of valence electrons in $H_3O^+ = (3 \times 1) + 6 - 1 = 8$. After putting in the single bonds and distributing the lone pair of electrons, the Lewis structure of H_3O^+ is shown. There are three bond pairs and one lone pair. Since *lp-lp* repulsion is greater than *lp-bp* repulsion, H_3O^+ has **pyramidal structure** (*i.e.* distorted tetrahedral with one lone pair).



4. NH_4^+ (Ammonium ion). $_7N = 1s^2\ 2s^2\ 2p^3$; $_1H = 1s^1$

Total number of valence electrons in $NH_4^+ = 5 + (4 \times 1) - 1 = 8$.

After putting in the single bonds and distributing the lone pair of electron, the lewis structure of ammonium ion is shown. There are four bond pairs and no lone pair. As there are only bond pairs, they will tend to keep themselves at maximum distance apart which is possible only in a regular tetrahedron. Thus, ammonium ion has a regular tetrahedral structure with each bond angle equal to 109°28′.



$$\ddot{N}H_3 + H^+ \longrightarrow \overset{+}{N}H_4$$

5. XeF_6 (Xenon hexafluoride)

$_{54}Xe = [Kr]^{36}\ 4d^{10}\ 5s^2\ 5p^6\ 5d^0$

$_9F - 1s^2 2s^2\ 2p_x^{\ 2}\ 2p_y^{\ 2}\ 2p_z^{\ 1}$

After putting in the single bonds between Xe and F-atoms, the lewis structure of XeF_6 is is shown. There are six bond pairs and one lone pair. Since *lp-bp* repulsion > *bp-bp* repulsion, there is some distortion in the shape of the molecule. Thus, XeF_6 has *distorted pentagonal bipyramidal structure* with one lone pair of electrons.

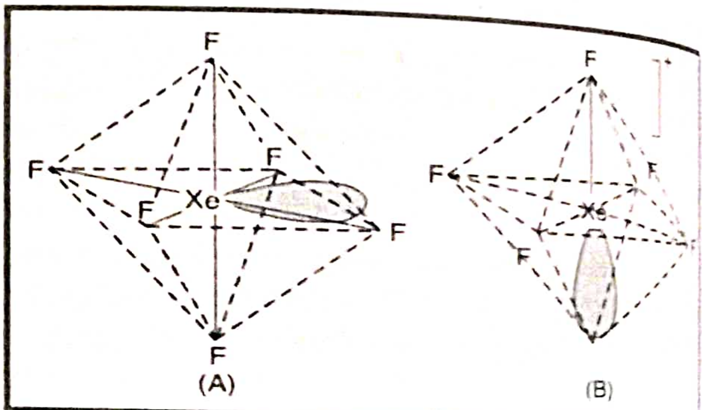


Fig. 1.12 (A) Distorted octahedral structure of XeF_6. (B) Structure of $[XeF_5^+]$.

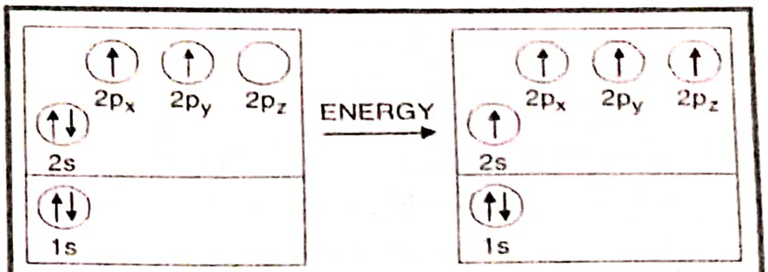
The crystal structure of XeF_6 reveals that it exists as $[XeF_5]^+\ F^-$ in the solid state. Hence, one F^-

ion is bridged with pyramidal cation. The non-bonding lone pair of electrons occupy the central position of one face of octahedron. As a result, the F-atom present at the corners of this face are repelled away. In this compound, Xe atom is sp^3d^3 hybridised.

HYBRIDISATION

According to orbital concept of covalent bonding, covalency of an element is equal to the number of partially filled orbitals in an atom of carbon in the ground state, *i.e.* $1s^2 2s^2 2p_x^1\ 2p_y^1$ [Fig. 2.13(*a*)], there are two partially filled or half filled orbitals (having one electron each). Therefore, carbon should be divalent in its compounds. However, carbon is tetravalent in its compounds such as CH_4, CCl_4, etc.

It is assumed that the carbon combines with other elements in the excited state when its configuration is $1s^2 2s^1 2p_x^1\ 2p_y^1 2p_z^1$ [Fig. 2.13(*b*)].



(a) Electronic configuration of carbon in ground state

(b) Electronic configuration of carbon in the excited state

Fig. 2.13 Electronic configuration of carbon in ground and excited state.

In order to have the electronic configuration $1s^2 2s^1 2p_x^1 2p_y^1 2p_z^1$ one electron from 2*s* orbital of carbon is to be promoted to the vacant $2p_z$ orbital by supplying energy. After the promotion, we have four half-filled orbitals which are available for bond formation.

The energy released due to the formation of two additional bonds compensates the energy required for promotion of the 2*s* electron.

Need for Hybridization. Consider the formation of methane (CH_4) from carbon. Four C – H bonds in case of methane are formed by the overlap of four partially filled orbitals of carbon with the four partially filled orbitals of four hydrogen atoms as shown in fig. 2.14.

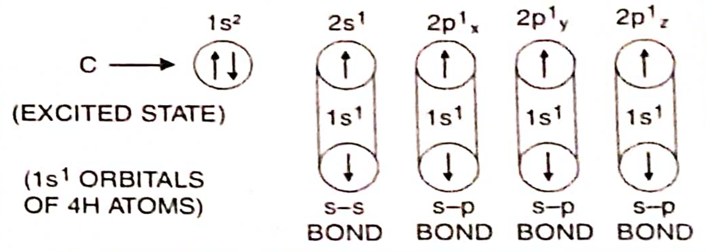


Fig. 2.14 Formation of Methane.

In the excited state of carbon, *s* and *p* orbitals have different energies. Consequently, four bonds of the carbon must be of two types. Three of the bonds should be of one type (*s*- *p* bonds) while fourth bond should be of a different type (*s*-*s* bond). However, experimental evidence indicates that all the four bonds in case of CH_4 are equivalent. To explain the equivalence of all the four bonds in case of CH_4, the concept of **hybridization** is used. The concept of hybridization is also useful to explain the observed values of angles.

Hybridization is the concept of intermixing of the orbtials of an atom having nearly the same energy to give exactly equal number of hybridised orbitals with same energy, identical shapes and symmetrical orientations in space.

The new equivalent orbitals formed are known as the hybrid orbitals or hybridized orbitals. Hybrid orbitals have properties entirely different from the properties of the original orbitals from which they have been obtained.

The phenomenon of hybridization involves the following two steps :

(*i*) **Promotion or excitation.** The carbon atom in the ground state has the configura $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^0$. It absorbs some energy when an electron from $2s$ orbital is promoted to the $2p_z$ orbitals. Thus, the configuration in the excited state is $1s^2 2s^1 2p_x^1 2p_y^1 2p_z^1$.

(*ii*) **Reorientation.** The orbitals containing four unpaired electrons rearrange themselves in altogether new order. It gives rise to the hybrid orbitals which are identical among themselves.

Types of Hybridization. Hybridization involved in case of carbon (depending upon the number of half-filled atomic orbitals taking part in it) is of three different types :

(*i*) sp^3 (*Tetrahedral*) *hybridization*

(*ii*) sp^2 (*Trigonal*) *hybridization*

(*iii*) *sp* (*Linear*) hybridization

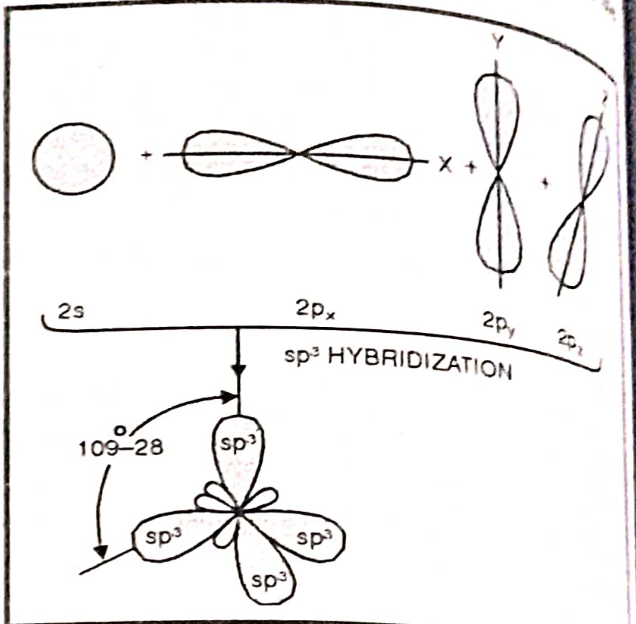


Fig. 2.15 Orientations of sp^3 hybrid orbitals.

(*i*) sp^3 **(Tetrahedral) hybridization.** One $2s$-orbital and three $2p$-orbitals of excited carbon get intermixed to form four sp^3 hybrid orbitals. This phenomenon is called sp^3 hybridization.

sp^3 hybridization, involving one spherical (non-directional) $2s$-orbital and three dumbell-shaped (directional) p-orbitals which are oriented along three axes at right angles to each other and gives four equivalent hybrid orbitals. These hybrid orbitals are directed at an angle of 109 28′ with respect to one another. These orbitals arrange themselves in the form of a regular tetrahedron (Fig. 2.15). Therefore, the hybridization is also known as **tetrahedral hybridization.** Each sp^3 hybrid orbital has 25% s-character and 75% p-character. It may be noted that hybrid orbitals consist of two lobes, one of which is quite large while the other is small. However, for the sake of simplicity, sometimes only major lobes are shown in molecules involved.

Simple molecules involving sp^3 hybridization of carbon atom are methane and ethane.

1. Formation of Methane. In methane, the four half-filled orbitals of carbon (before taking part in bond formation), mix up their energies and redistribute equally to give four new and absolutely equivalent sp^3 hybrid orbitals which are directed at an angle of 109° 28′ with respect to one another (Fig. 2.15).

The four sp^3 hybrid orbitals overlap with $1s$-orbitals of four hydrogen atoms to form four s-sp^3 sigma bonds [Fig. 2.16(*a*)]. The four bonds in CH_4 are directed towards the four corners of a regular tetrahedron [Fig. 2.16(*b*)]. Bond length of each C–H bond is 1.09Å or 109 pm and

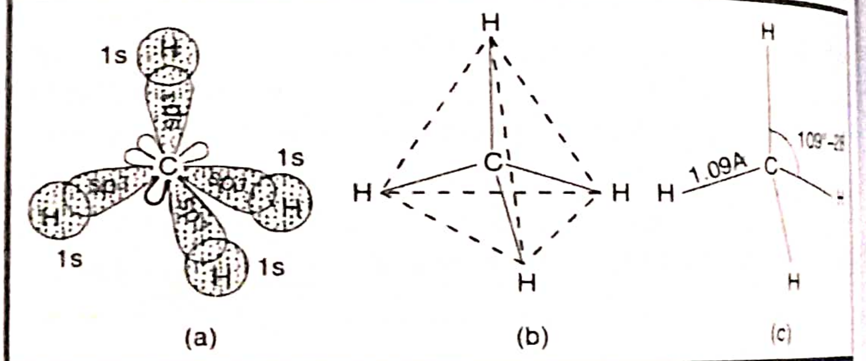


Fig. 2.16 Formation and structure of Methane.

linear structure and the two bonds in them are identical. The ground state configuration of Be is as shown in Fig. 2.25(a).

In order to explain the formation of two equivalent bonds by beryllium, we may assume that one 2s electron is excited to the vacant higher energy 2p-orbital. The excited state electronic configuration of beryllium atom is as shown in fig. 2.25(b).

The 2s and 2p atomic orbitals then hybridize to form two equivalent *sp* hybrid orbitals which are at an angle of 180° w.r.t. each other (Fig. 2.25). These two equivalent *sp* hybrid orbitals are used to make two identical bonds in beryllium compounds.

A simple example involving *sp*-hybridization of Be is BeF_2.

Hybridization of Elements Involving d-orbitals

The elements of second period do not have *d*-orbitals. These are thus unable to extend their octet. The elements of third period (say P, S etc.) contain *d*-orbitals and hence can extend their octet. Since the energy of 3s and 3p orbitals is approximately same as that of 3*d* orbitals, these undergo hybridization to form dsp^2, sp^3d, sp^3d^2, sp^3d^3 etc. hybrid orbitals depending upon the nature of the compound. Let us discuss the geometries of some compounds involving *d*-orbitals.

1. sp^3d-hybridisation. When one *s*, three *p* and one *d*-orbitals (of the central atom of a compound) of nearly the same energy intermix, we get five resultant equivalent orbitals called **sp^3d hybrid orbitals** (Fig. 2.26). These hybrid orbitals point towards the five corners of a trigonal bipyramidal geometry. Out of these five sp^3d hybrid orbitals, three are directed towards the three corners of an equilateral triangle while the remaining two are at right angles to the plane of the first three orbitals.

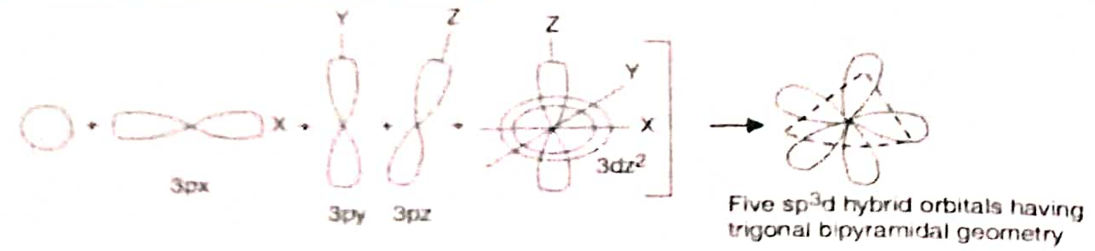


Fig. 2.26 sp^3d hybridisation.

Common examples of compounds involving sp^3d hybridisation of central atom are PF_5 and PCl_5.

Geometry of PCl_5 molecule. The electronic configuration of phosphorus and chlorine in the ground state are :

$_{17}Cl$: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3px^2\ 3py^2\ 3pz^1$

15 P : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3px^1\ 3py^1\ 3pz^1$

To explain the pentavalency of phosphorus, five electrons should be unpaired. For this, the electronic configuration of phosphorus in the excited state is considered. Here one of the 3s electrons is promoted to the 3d orbital and

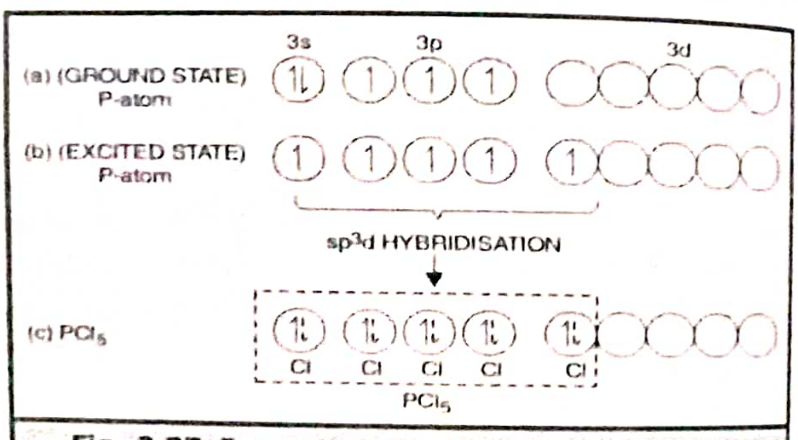


Fig. 2.27 Formation of PCl_5 molecule involving sp^3 of hybridisation.

of nearly same energy intermix to give resultant equivalent orbitals called sp^3d hybrid orbitals. These hybrid orbitals are directed towards the five corners of a trigonal bipyramidal geometry. Each of the sp^3d hybrid orbital overlaps with $3p$-orbital (half filled) of Cl atom forming five P-Cl sigma bonds (Fig. 2.28).

Out of these five sp^3d hybrid orbitals, three are directed towards the three corners of an equilateral triangle making an angle of 120° with one another. The bonds formed by these orbitals are called equitorial bonds. These are marked as '*e*' in Fig. 2.32. The remaining two hybrid orbitals are at right angles (90°) to the plane of first three orbitals and the bonds formed by these orbitals are called axial bonds and are marked '*a*' in Fig. 2.28.

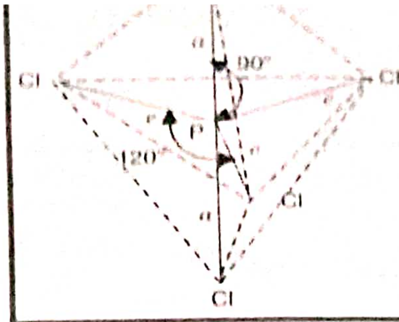


Fig. 2.28 Geometry of PCl_5.

It is important to note that the shape of PCl_5 is not completely regular since all the bond angles and bond lengths are not equal. The angle between two equatorial bonds is 120° and the angle between an axial bond and an equatorial bond is 90°. The axial bonds are longer than the equatorial bonds and bond length of each P-Cl equatorial bond is 204 pm and that of each axial P-Cl bond is 219 pm. The longer bond length of axial bonds is due to the fact that each axial bond pair is repelled by three equatorial bond pairs at 90°, whereas each equatorial bond pair is repelled by two axial bond pairs at 90°. Thus the repulsion exerted on the axial bond pair is more. Hence the bond length of axial bonds is longer. Axial bonds due to their longer bond length are weaker than equatorial bonds. **Due to the presence of weaker bonds, PCl_5 molecule is quite reactive.**

Since P atom in PCl_5 is sp^3d hybridised, PCl_5 molecule has trigonal bipyramidal geometry.

Geometry of PF_5 molecule. Geometry of PF_5 is similar to that of PCl_5 with the difference that sp^3d hybrid orbital of P-atom overlaps with half-filled $2pz$-orbitals of F-atom ($1s^2\ 2s^2\ 2p_x^2\ 2p_y^2\ 2p_z^1$) and not with $3p_z$ orbitals as in the case of Cl-atom $(Ne)^{10}\ 3s^2\ 3p_x^2\ 3p_y^2\ 3p_z^1]$

Geometry of SF_6 molecules: sp^3d^2 hybridisation. When one *s*, three *p* and two *d*-orbitals of nearly same energy intermix, we get resultant equivalent orbitals called sp^3d^2 hybrid orbitals. These orbitals are directed towards the six corners of an octahedron and are at 90° to each other. The shape of SF_6 molecule will help to understand this type of hybridisation.

The electronic configuration of sulphur in the ground state is

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

In the excited state, the electrons in the $3s$ and $3px$ orbitals get unpaired as follows :

$${}_{16}S\ (\text{excited}) :\ 1s^2,\ 2s^2,\ 2p^6,\ 3s^1,\ 3p_x^1,\ 3p_y^1,\ 3p_z^1\ (3d_x^2 - y^2)^1\ \ (3dz^2)^1$$

The six half filled orbitals of sulphur get mixed up to form six hybrid orbitals, called sp^3d^2 hybrid orbitals. These orbitals are directed towards the six corners of a regular octahedron and are at 90° to each other. The central atom should carry no lone pair of electrons.

In SF_6 molecule, six sp^3d^2 hybrid orbitals overlap with half filled orbitals of fluorine atoms to form six S–F sigma bonds as shown in Fig. 2.29. Thus SF_6 molecule has octahedral shape.

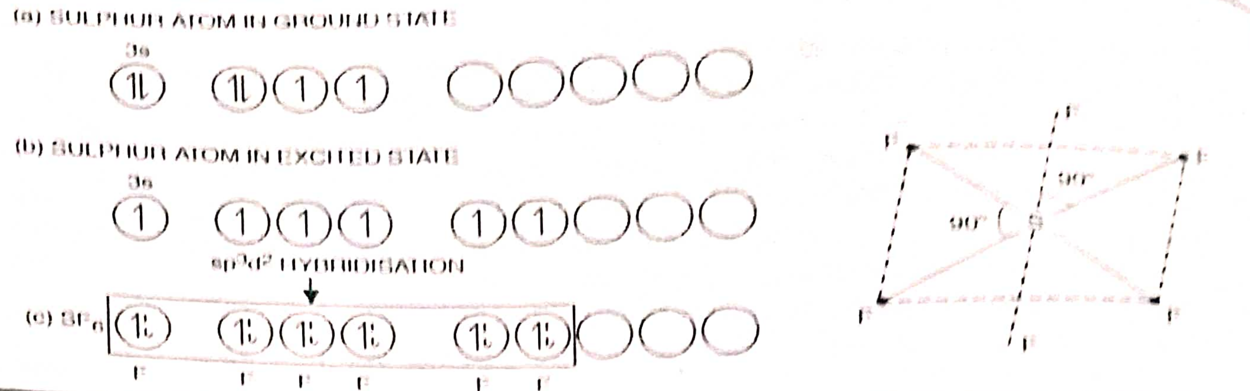


Fig. 2.29 Formation of SF_6 molecule involving sp^3d^2 hybridisation.

For number of theoratical reasons and considerations of energetics, the explanation for bonding in terms of hybridisation in case of hypervalent molecules like PCl_5 and SF_6 is not accepted. Now the bonding in such molecules is best explained in terms of molecular orbitals.

It is important to note that in most of the cases, the hybrid orbital are equivalent and symmetric. For example, four sp^3 hybrid orbitals are directed to the four corners of a regular tetragon. Also six d^2sp^3 hybrid orbitals are directed to the six corners of a regular octahedron. But in case of sp^3d hybridisation (as in PCl_5), the hybrid orbitals are not exactly equivalent. Three orbitals (taken as sp^2) form one set of equivalent orbitals and two (taken as dp perpendicular to the plane of sp^2 orbitals) form another set. Here sp^2 orbitals are called equitorial orbitals whereas dp orbitals are axial). Equitorial bonds form stronger bonds compared to axial bonds.

Table 2.9 Types of hybridisation and shapes of Molecules

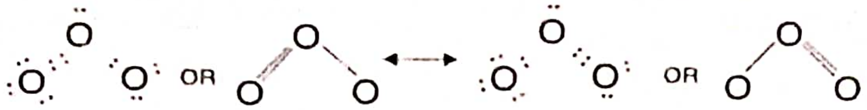
Number of outer orbitals	Shape	Hybridisation	Bond angle
2	Linear	sp ($BeCl_2$, C_2H_2, $HgCl_2$) etc.	180°
3	Plane triangular	sp^2 (BCl_3, C_2H_4, Graphite)	120°
4	Tetrahedron	sp^3 (CH_4, CCl_4, Dimond)	109° 28′
5.	Trigonal bipyramidal)	dsp^3 (PCl_5)	90° and 120°
6	Octahedron	d^2sp^3 (SF_6)	90°

CONCEPT OF RESONANCE

For most covalent molecules, there is a unique single electron dot formula or Lewis structure that is able to explain the known properties of the substance. However, in case of certain comp[illegible]ore than one structure can be written but none of them is able to explain all the known properti[illegible]pound. For example, we can write two electron dot structures for the O_3 molecule. In th[illegible] oxygen has an octet of electrons. Each structure depicts one O=O double b[illegible]

CONCEPT OF RESONANCE

For most covalent molecules, there is a unique single electron dot formula or Lewis structure that is able to explain the known properties of the substance. However, in case of certain compounds, more than one structure can be written but none of them is able to explain all the known properties of the compound. For example, we can write two electron dot structures for the O_3 molecule. In these structures, each oxygen has an octet of electrons. Each structure depicts one O = O double bond and one O – O single bond. Since double bonds are shorter in length than single bonds, the two bond lengths in O_3 molecule should be different. However, it has been found experimentally that the two bond lengths are equal (1.28 Å or 128 pm). The bond length is intermediate between O – O bond (1.48 Å) and O = O bond (1.21 Å). Thus, none of the above two structures represents the actual structure of the molecule. In such cases where more than one structure can be written for a compound but none of them is able to explain the known properties of the compound completely, the different structures written are known as **resonating** or **contributing** or **canonical structures**. This phenomenon is known as **resonance**.



It is important to know that resonating structures have no physical reality. Resonating structures are only imaginary. The need for resonance concept arises because properties of many molecules cannot be explained on the basis of a single Lewis structure.

(i)

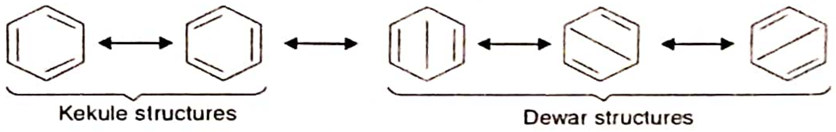
(ii)

The actual structure known as the **resonance hybrid** lies somewhere inbetween these structures. However, we have no physical means to represent that structure on the paper. The resonance hybrid may be represented by putting double headed arrows inbetween the various contributing structures as illustrated below for ozone.

The **resonance hybrid** neither oscillates between the contributing structures nor it consists of a mixture of the contributing forms. It is an **entirely new** and **individual** structure.

It may be noted that different resonating structures of a molecule have same relative arrangement of their atoms. However, they differ in the arrangment of electrons.

Individual structures of similar energy contribute equally to the resonance hybrid. Resonating structures with higher energy also contribute to the resonance hybrid. However, the contribution of a canonical structure to the resonance hybrid decreases with increase in energy of a particular structure. For example, benzene is a resonance hybrid of the following structures :



Out of these, Kekule structures have lower energy and thus contribute more to the resonance hybrid.

Conditions for Resonance

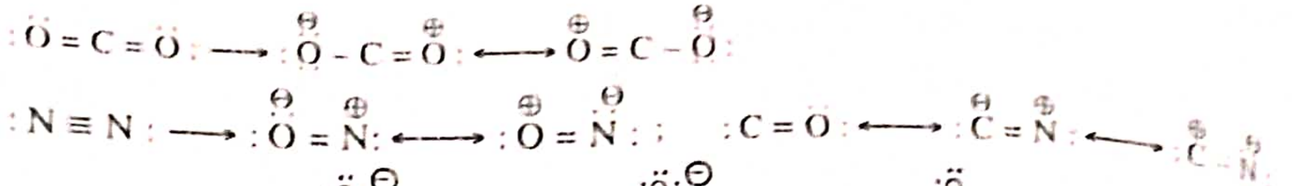
1. The different contributing structures should have the same position of the constituent atoms, though they may have different electronic arrangements.
2. The number of unpaired electrons must be the same in each contributing structure. We should not draw structures in a manner that one structure may not contain even a single unpaired electron and another contains two unpaired electrons.
3. The contributing structures should have nearly the same energy.
4. The bond lengths and bond angles should be closer to the real structure.
5. Those structures in which negative charge resides on the most electronegative atom and positive charge on the most electropositive atom will be closer to the true structure.
6. The contributing structures should be so written that unlike charges reside on neighbouring atoms. The contributing structures involving charge separation have little contribution to resonance hybrid.

7. The greater the number of covalent bonds, greater is the contribution of that resonating

8. The compounds exhibiting resonance must be planar in nature.

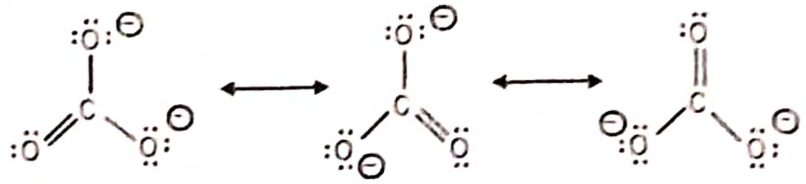
Some other important examples of compounds showing resonance are :

(*i*) **Inorganic Compounds**



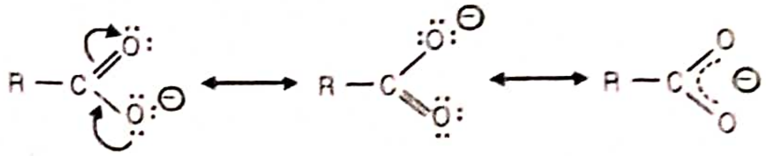
$:\ddot{O}=C=\ddot{O}: \longrightarrow :\overset{\ominus}{\ddot{O}}-C=\overset{\oplus}{O}: \longleftrightarrow \overset{\oplus}{O}=C-\overset{\ominus}{\ddot{O}}:$

$:N\equiv N: \longrightarrow :\overset{\ominus}{O}=\overset{\oplus}{N}: \longleftrightarrow :\overset{\oplus}{O}=\overset{\ominus}{N}:: \quad :C=O: \longleftrightarrow :\overset{\ominus}{C}=\overset{\oplus}{N}: \longleftrightarrow :\overset{\oplus}{C}-\overset{\ominus}{N}:$

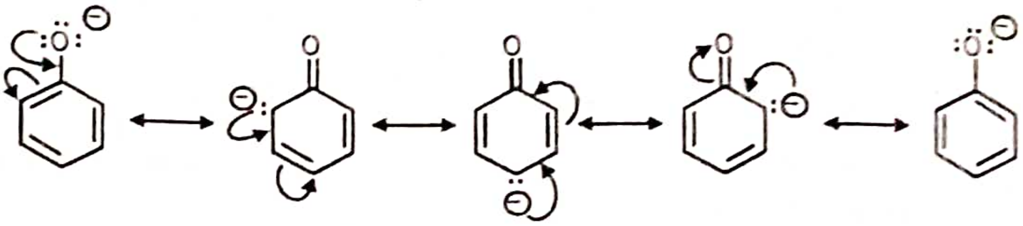


Carbonate

(*ii*) **Organic Compounds**



Carboxylate ion



Phenate ion

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

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

MOLECULAR ORBITAL THEORY (MOT)

According to molecular orbital theory, the atomic orbitals of the bonded atoms lose their identity. They mix up or coalesce to form the molecular orbitals. Molecule is regarded as the polynuclear structure. The space around the nuclei is distributed into molecular orbitals. Electrons are filled in these molecular orbitals according to the rules which are similar to those governing the filling of atomic orbitals.

Molecular orbitals may be defined as the regions in space (embracing the nuclei of all the bonded atoms in a molecule) in which an electron is most likely to be found.

The salient features of the molecular orbital theory are given below :

1. Molecular orbitals embrace the nuclei of all the bonded atoms in a molecule.
2. Molecular orbitals are obtained by combining atomic orbitals of comparable energies.
3. When a set of atomic orbitals combine to form molecular orbitals, the number of molecular orbitals equals the number of atomic orbitals.
4. Two atomic orbitals, (one from each atom) combine to produce two molecular orbitals. One of these possesses lower energy than energy of either atomic orbitals and the other has energy higher than the energy of atomic orbitals.

The molecular orbital with lower energy is called bonding molecular orbital (more stable). The molecular orbital with higher energy is called antibonding molecular orbital, (Fig. 2.30).

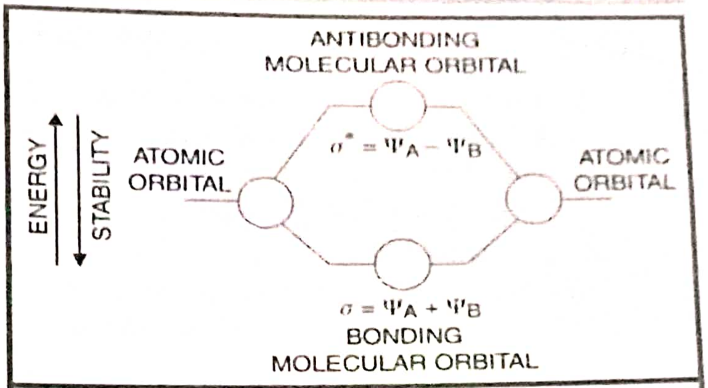


Fig. 2.30 Bonding and Anti-bonding molecular orbitals.

5. Each molecular orbital can accommodate maximum of two electrons with opposite spins.
6. The shape of molecular orbitals depends upon the shapes of combining atomic orbitals.
7. The molecular orbitals are arranged in the increasing order of their energies. These are filled in the same way as the atomic orbitals are filled in case of atoms.
8. Electron pairing in degenerate* molecular orbitals cannot take place unless each degenerate molecular orbital is singly occupied (Hund's rule).

The main points of difference between atomic orbitals and molecular orbitals are summarised below :

	Atomic Orbitals		Molecular Orbitals
1.	These exist around the nucleus of a single atom.	1.	These exist around all the nuclei of bonded atoms in a molecule.
2.	Their existence is because of the inherent property of the atoms.	2.	These are formed by the combination of atomic orbitals of comparable energies.
3.	These have simple shapes.	3.	These have complex shapes.
4.	Atomic orbitals are designated as *s*, *p*, *d* and *f*.	4.	Molecular orbitals are designated as σ, π, δ.... and σ^*, π, δ^* ... etc.

Table 2.10 Difference between Bonding and Antibonding Molecular Orbitals

	Bonding Molecular Orbital		Antibonding Molecular Orbital
1.	It is formed by the addition overlap of atomic orbitals $\psi_{M.O} = \psi_A + \psi_B$. where ψ_A = wave function of atomic orbital A. ψ_B = wave function of atomic orbital B.	1.	It is formed by the subtraction overlap of atomic orbitals $\psi^*_{M.O} = \psi_A - \psi_B$
2.	It has higher electron density in the region between the two nuclei.	2.	It has zero electron density in the plane between the two nuclei. Thus, there is a nodal plane in the antibonding molecular orbitals.
			[illegible] higher electron density than the

LINEAR COMBINATION OF ATOMIC ORBITALS

It is very difficult to solve Schrodinger wave equation for systems having more than one electron. Thus, a new approximation called *linear combination of atomic orbitals* (LCAO) is used to explain bonding in molecules. This theory was developed by Hund and Mulliken. *Various postulates of this theory* are

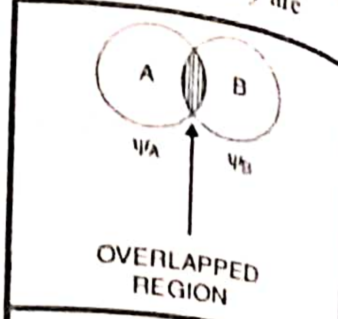


Fig. 2.31 Overlapping of atomic obitals.

(*i*) A molecular orbital is formed by linear combination of atomic orbitals of bonded atoms.

(*ii*) The atomic orbitals of constituent atoms (having same or approximately same energy) *combine in an additive* fashion to form molecular orbitals. Consider two atoms A and B which form a molecule, AB. Let wave function of atom, A = ψ_A, wave function of atom, B = ψ_B

When atomic orbitals, ψ_A and ψ_B (accommo-dating valence electrons) of atoms A and B overlap, the valence electrons are found in overlapped region (fig 2.31).

(*iii*) All the electrons of the atoms A and B are considered to move along the entire molecule under the influence of all the nuclei.

(*iv*) The molecule is considered different from the atoms which make it.

(*v*) The energy of different molecular orbitals formed is different. It is in accordance with the Aufbau principle.

(*vi*) A molecular orbital can have maximum of two electrons. These two electrons have opposite spins. This is in accordance with the Pauli's exclusion principle.

(*vii*) The wave function of an electron in a molecule is called molecular orbital.

(*viii*) The wave function (ψ_{AB}) of the molecular orbital is given by the relation :

$$\psi_{AB} = C_A\,\psi_A + C_B\,\psi_B \qquad ...(i)$$

where C_A and C_B are the mixing co-efficients. The values of C_A and C_B are so selected that the energy of the molecular orbital becomes the least.

Types of Molecular Orbitals. Consider the bonding in homonuclear molecules. In such cases, the values of C_A and C_B (mixing co-efficients) are same. Thus :

$$C_A^2 = C_B^2 \qquad \text{or} \qquad C_A = \pm\, C_B$$

$$\therefore \qquad C_A = +\, C_B \qquad \text{or} \qquad C_A = -\, C_B \qquad ...(ii)$$

For similar atoms, $C_A = C_B = 1$.

Substituting the value of C_A and C_B from equation (*ii*) in equation (*i*) we get following two molecular orbitals as a result of two types of combinations

$$\psi_{AB} = \psi_A + \psi_B \qquad [\because C_A = +\,C_B = +1]$$

$$\psi_{AB}^{*} = \psi_A - \psi_B \qquad [\because C_A = -\,C_B = -1]$$

where ψ_{AB} = Bonding molecular orbital ; ψ^{*}_{AB} = Antibonding molecular orbital.

In order to get stable molecular orbitals, there should be effective overlapping of atomic orbitals. The *conditions necessary for overlapping are given below.*

(*i*) The relative energies and symmetry of atomic orbitals, ψ_A and ψ_B should be same or approximately same.

(*ii*) The wave functions of atomic orbitals (ψ_A and ψ_B) of same sign should overlap *i.e.*, + ve with + ve and – ve with – ve should overlap.

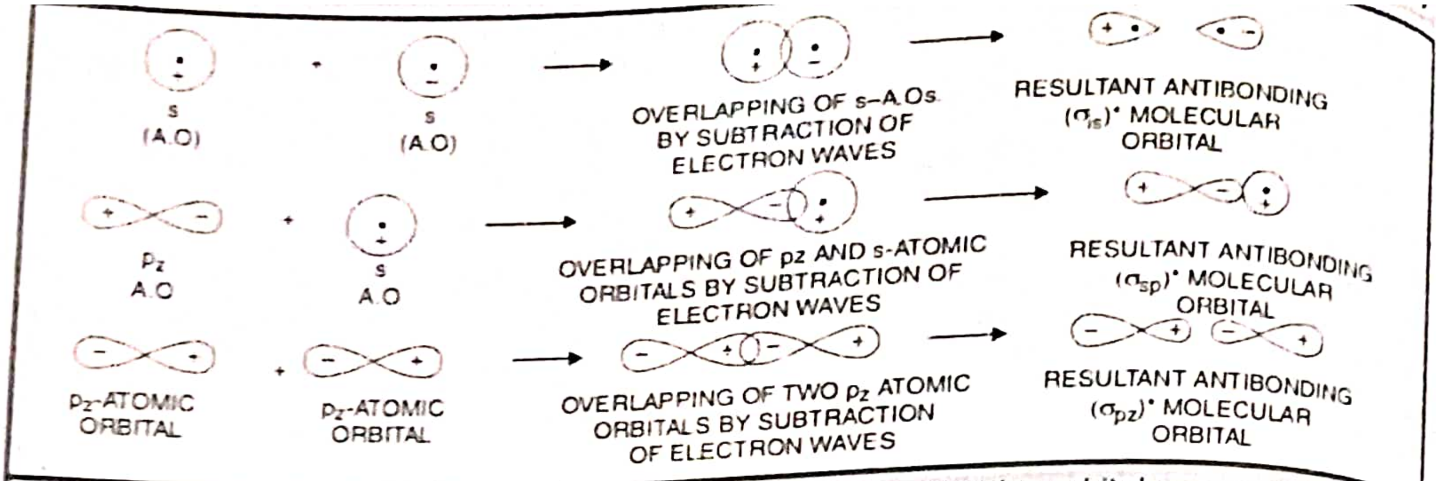


Fig. 2.37 Formation of σ^*-antibonding molecular orbitals.

The characteristics of this molecular orbital are :

(*i*) The electron in this molecular orbital is available in such regions which are away from each nuclei. Thus, there is zero electron density (nodal plane) between the two nuclei.

(*ii*) Its energy is higher than that of the 1*s*-atomic orbital from which it is made of. Thus, it is called antibonding molecular orbital.

(*iii*) It is symmetric to rotation about the inter-nuclear axis *i.e.*, it remains unaffected when rotated through 180° (Fig. 2.38). Such an orbital is called sigma (σ^*) antibonding molecular orbital (σ_{1s}^*).

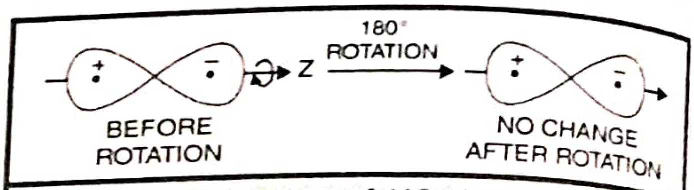


Fig. 2.38 Rotation of MO through 180°.

The linear combination of atomic orbitals which are obtained by the addition and subtraction overlap of 2s-atomic orbitals are similar to 1s-atomic orbitals.

A sigma (σ) molecular orbital is also formed by the addition or subtraction overlap of p_z-atomic orbitals along the inter-nuclear axis (Fig. 2.39).

Such orbitals are cylindrically symmetrical around the bond axis.

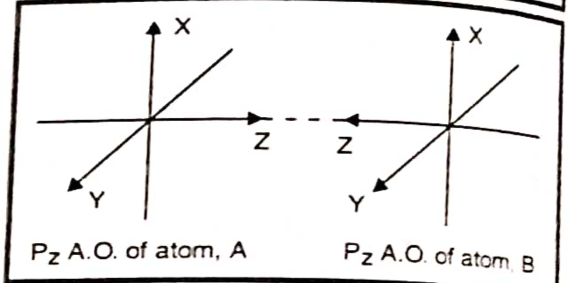


Fig. 2.39 Coordinate systems used to show overlapping of 2*p*-atomic orbitals.

The molecular orbital which is formed by the addition overlap of p_z-atomic orbitals is represented by σ_{pz} and is called σ-bonding molecular orbital. The molecular orbital formed by the subtraction overlap of *p*-atomic orbitals is represented by $\sigma_{pz}{}^*$ and is called σ^*-antibonding molecular orbital (Fig. 2.39).

Pi (π) molecular orbitals π and π^* molecular orbitals. *A molecular orbital which results from the sidewise or lateral overlap of two p-atomic orbitals perpendicular to internuclear axis is known as pi* (π) molecular orbital.

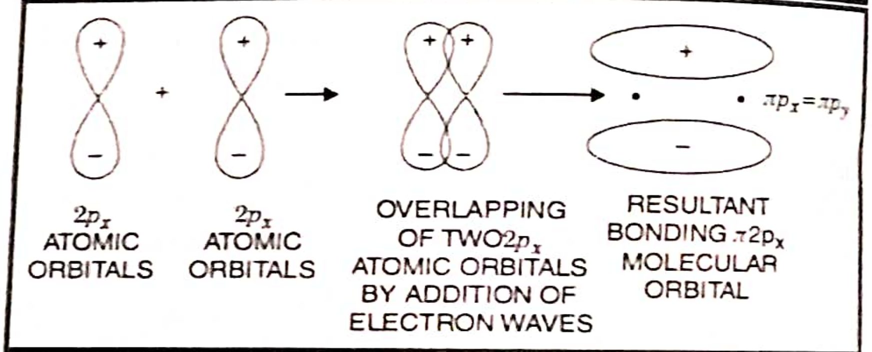


Fig. 2.40 Formation of p-bonding molecular orbitals.

π-bonding molecular orbitals are formed by the sidewise overlap of two p-orbitals having the same sign. These are designated as π_{px} or π_{py} depending upon the use of p_x or p_y orbitals in bond formation as shown in Fig. 2.40.The sideways addition overlap of $2p_x$ atomic orbitals of two atoms to form bonding molecular orbital is shown.

π-antibonding molecular orbitals are formed by the sidewise overlap of two p-orbitals having opposite sign. These are designated as π_{px}^* or π_{py}^* depending upon the use of p_x or p_y atomic orbitals in overlap (Fig. 2.41). The side ways subtraction overlap of $2p_x$ atomic orbitals of two atoms to form antibonding molecular orbital is shown below.

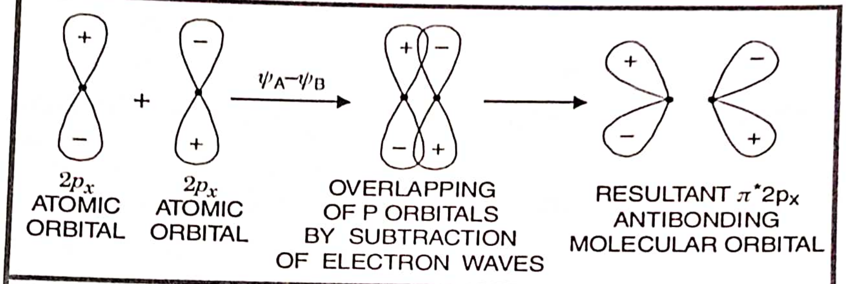


Fig. 2.41 Formation of π^*2p_x anti-bonding molecular orbitals.

It is important to note that the *positive* and *negative* signs as indicated in the figure, are concerned only with the sign of the wave function, and nothing else, i.e., these do not represent charge.

Characteristics of p-bonding molecular orbital

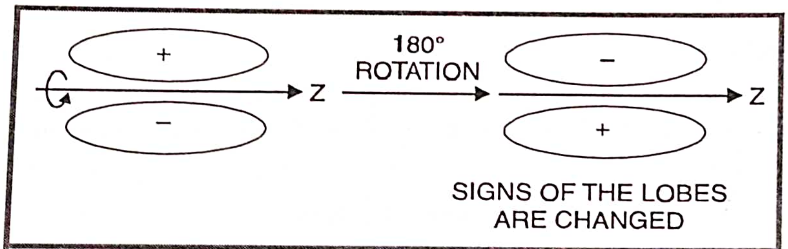


Fig. 2.42 Rotation of MO through 180°.

(*i*) It is formed when p_x (or p_y) atomic orbitals of same algebraic sign overlap.

(*ii*) It has (+) lobe above the Z-axis and (–) lobe below the Z-axis.

(*iii*) It is antisymmetric to rotation about the molecular axis *i.e.*, the signs of lobes change when rotated through 180° (Fig. 2.42).

(*iv*) It is represented by π_{px} (or π_x). When p_x atomic orbitals are used, the MO is represented by π_y (or π_{py}). The energy of π_{2px} is equal to that of π_{2py}. These two MOs are, hence, called **degenerate**.

Table 2.11. Comparison of sigma and pi-overlap

	σ-overlap		π-overlap
1.	This type of overlap involves head on overlapping of two atomic orbitals along the internuclear axis.	1.	This type of overlap involves lateral (or sidewise,) overlap of two atomic orbitals, perpendicular to the internuclear axis.
2.	The overlapped region is maximum (Fig. 2.43).	2.	The overlapped region is minimum (Fig. 2.43).
3.	It results in a strong bond.	3.	It results in a weak bond.

The letters σ and π are used to characterise different shapes of electron clouds in molecules (MO's). In case of atoms the letters s, p, d and f are used to characterise different shapes of electron clouds of atoms (AO's).

Sigma (σ) and pi (π) molecular orbitals are discussed below:

Sigma (σ) and σ* Molecular Orbitals

Sigma molecular orbitals. *A molecular orbital which is formed from the head on overlap of two s-atomic orbitals or head to head overlap of an s and p-atomic orbitals or head to head overlap of two p-atomic orbitals* is known as **sigma molecular orbital.**

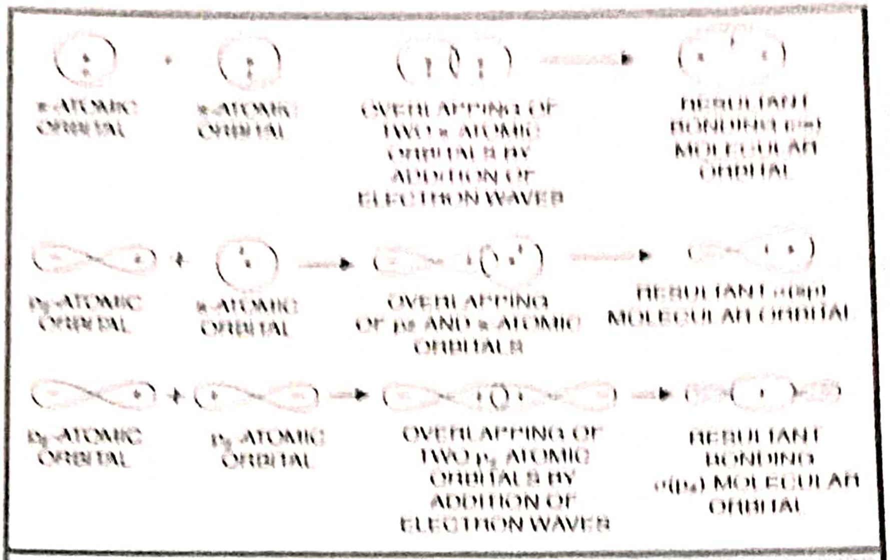


Fig. 2.35 Formation of σ-bonding molecular orbitals.

σ-bonding molecular orbitals are formed by the combination of atomic orbitals having the same sign. They are designated as σ_s, σ_{sp} and σ_p depending upon the nature of the atomic orbitals from which these are formed (Fig. 2.35). Formation of σ-bonding M.O. in H_2 molecule (formed from hydrogen atoms H_a and H_b) is represented by the following relation :

$$\psi_{MO} = N\,(\psi_{1sa} + \psi_{1sb})$$

[Here N = Normalising constant. $1s_a$ and $1s_b$ are the 1s orbitals of H-atoms, H_a and H_b respectively]

It has maximum electron density between the two nuclei.

The *characteristics of this molecular orbital are* :

(*i*) Its energy is lower than that of the 1s-atomic orbital from which it is made of. Thus, it is called bonding molecular orbital.

(*ii*) It is symmetric to rotation about the inter-nuclear axis (*i.e.*, it remains unaffected when rotated through 180°. (Fig. 2.36).

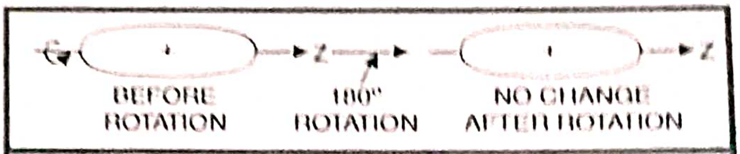


Fig. 2.36 Rotation of MO through 180°.

Such an orbital is called sigma (σ) bonding molecular orbital (σ_{1sb}).

(*iii*) The electron in this molecular orbital is under the influence of two nuclei. It is thus, more stable than that when present in atomic orbital.

σ-antibonding molecular orbitals are formed by the combination of atomic orbitals having opposite sign. They are designated as σ_s^*, σ_{sp}^* and σ_p^* depending upon the nature of the atomic orbitals from which they are formed as shown in Fig. 2.37. Formation of σ*-antibonding M.O. in H_2 molecule (formed from hydrogen atoms H_a and H_b respectively) is represented by the following relation:

$$\psi^*_{MO} = N'\,(\psi_{1sa} - \psi_{1sb})$$

[Here, N′ is another normalising constant. $1s_a$ and $1s_b$ are the 1s orbitals of H-atoms H_a and H_b respectively.

available MOs in correct energy order. This is easier for homonuclear diatomic molecules than for heteronuclear ones, and it is still more difficult for polynuclear molecules.

(a) Molecular orbital treatment of hamoatmic diatomic molecules (N_2 and O_2)

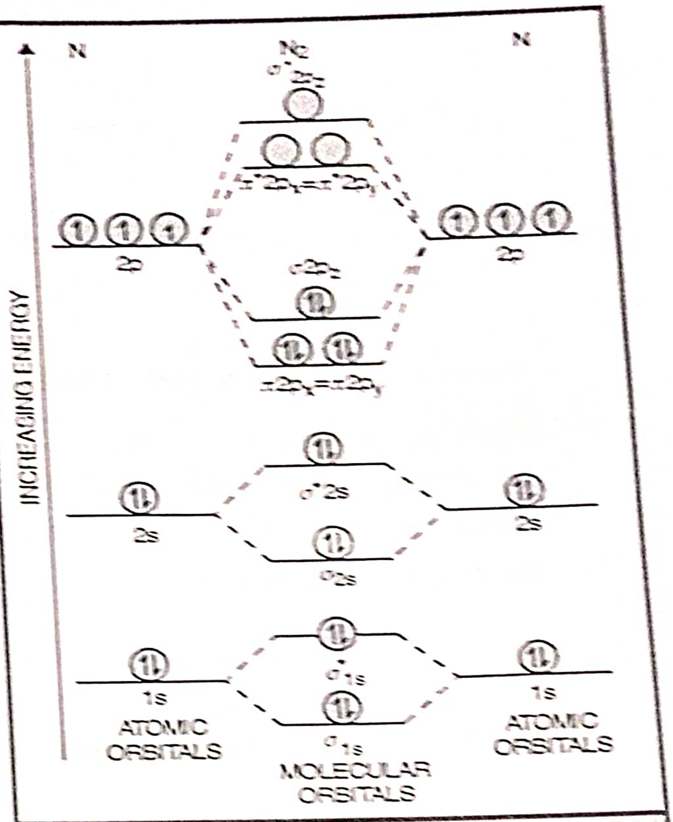


Fig. 2.49 MO Energy level diagram for N_2 molecule.

(*i*) **Nitrogen Molecule (N_2).** Nitrogen molecule is formed by the combination of atomic orbitals of two nitrogen atoms each having seven electrons ($1s^2\ 2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^1$).

$\therefore$ Number of electrons in N_2 molecule = 14.

These 14 electrons are filled in various molecular orbitals in the increasing order of their energies (aufbau principle) and on the basis of Hund's rule and Pauli's exclusion principle (two electrons of MO must have opposite spins) as shown in Fig. 2.49.

The important features of N_2 molecule are :

(*a*) **Electronic configuration**

$$N_2\ [(\sigma 1s)^2\ (\sigma^*\ 1s)^2\ (\sigma\ 2s)^2\ (\sigma^*\ 2s)^2\ (\pi_{2px})^2$$

$$= (\pi_{2py})^2\ (\sigma_{2pz}\ )^2$$

The correctness of this configuration* is proved by the fact that the odd electron in N_2^+ is present in sigma orbital (σ_{2pz}) according to the spectroscopic evidence.

The bonding and non-bonding effect of electrons of inner shell (*i.e.*, 1*s*) gets cancelled. These electrons are also represented as KK corresponding to the filled, first or K shells of both atoms.

Thus KK stands for $(\sigma 1s)^2\ (\sigma^*\ 1s)^2$ and the configuration may be represented as :

$$N_2\ [KK(\sigma 2s)^2\ (\sigma^*\ 2s)^2\ (\pi\ 2p_x)^2 = (\pi\ 2p_y)^2\ (\sigma 2p_z)^2$$

(*b*) **Bond order.** The bond order in N_2 molecule $= \frac{1}{2}\,[\,N_b - N_a] = \frac{1}{2}\,[8 - 2] = 3$

Thus the two nitrogen atoms in nitrogen molecule are linked by three covalent bonds *i.e.*, a triple bond.

(*c*) **Bond dissociation energy.** Bond dissociation energy of N_2 molecule is 945.0 kJ per mole. High bond dissociation energy of molecule which is, infact, the highest amongst diatomic molecules indicate that N_2 molecule is highly stable.

(*d*) **Bond length.** Bond length of N_2 is found to be 110 pm or 1.10 Å.

(*e*) **Magnetic behaviour.** N_2 molecule is found to be diamagnetic due to the absence of unpaired electrons.

N_2^+ (Dinitrogenyl cation). Number of electrons in N-atom = 7

Number of electrons in N^+ ion = 7 – 1 = 6

$\therefore$ Total number of electrons in N_2^+ ion = 7 + 6 = 13.

These 13 electrons are filled in various molecular orbitals in the increasing order of their energi (aufbau principle) and on the basis of Hund's rule and Pauli's exclusion principle.

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The bond order, stability and magnetic character of above species are given in the following table.

Species	Bond order	Stability	Magnetic Character
N_2	3	most stable	Diamagnetic
N_2^+	2.5	Less stable	Paramagnetic (due to one $\bar{e}$)
N_2^-	2.5	Less stable	Paramagnetic (due to one $\bar{e}$)
N_2^{-2}	2	Least stable	Paramagnetic (due to two unpaired electrons)

(*ii*) Oxygen molecule (O_2) : $_8O$: $1s^2\ 2s^2\ 2px^2\ 2py^1\ 2pz^1$

Each oxygen atom has eight electrons. Therefore, there are sixteen electrons in oxygen molecule. Due to the combination of atomic orbitals of the two atoms, ten molecular orbitals are formed. These are filled (by the available electrons) in the increasing order of their energies (aufbau principle).

The configuration of O_2 is :

$O_2 : (\sigma_{1s})^2\ (\sigma^*\ 1s)^2)\ (\sigma_{2s})^2\ (\sigma^*\ 2s)^2\ (\sigma_{2p_z})^2$
$(\pi 2p_x)^2\ = (\pi\ 2p_y)^2\ (\pi^*\ 2p_x)^1 = (\pi^*\ 2p_y)^1$.

Last two molecular orbitals are half filled. It is due to Hund's rule. From the above configuration, we have

$$N_b = 10,\ N_a = 6$$

∴ Bond order

$$= \frac{1}{2}(N_b - N_a) = \frac{1}{2}(10 - 6) = 2.$$

Hence, there is a double bond in oxygen molecule. Due to the presence of two unpaired electrons, it is paramagnetic.

Molecular orbital diagram of O_2 is shown in Fig. 2.50.

Bond dissociation energy of O_2 molecule is 498 kJ mol^{-1} and its bond length is 121 pm.

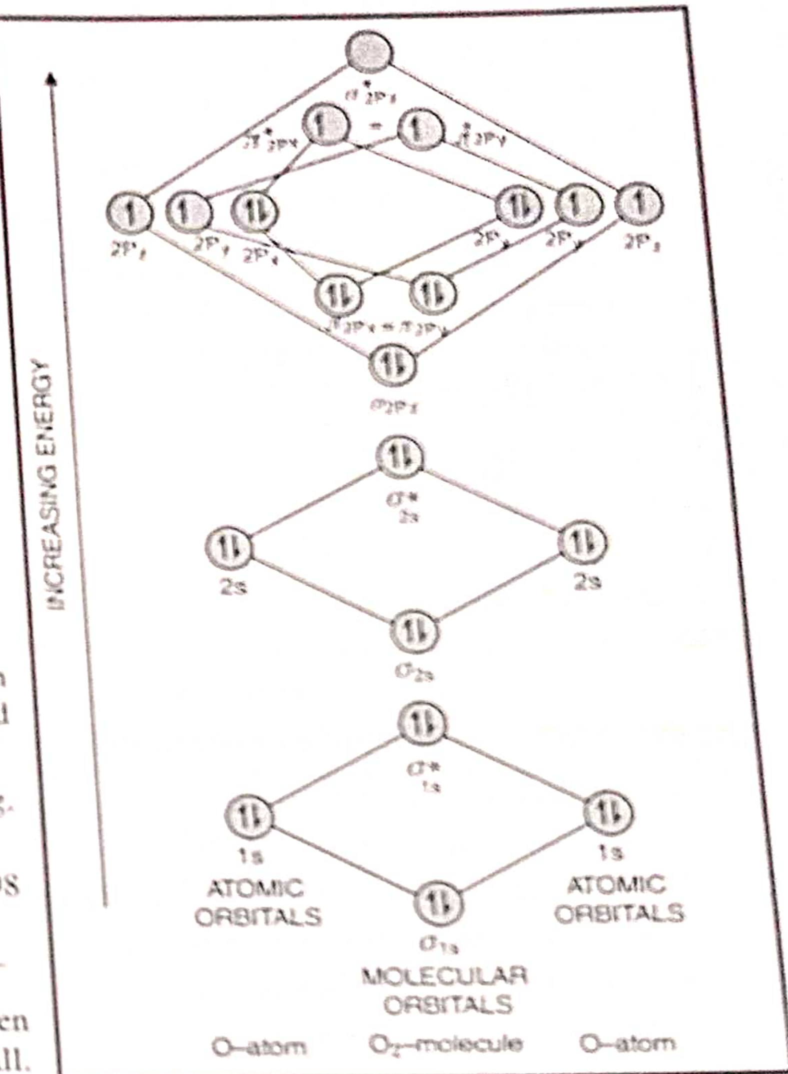


Fig. 2.50 Molecular orbital diagram of O_2.

O_2^+-Ion (Dioxygenyl ion) : $O_2 \longrightarrow O_2^+ + e^-$

This ion has one electron less than that in oxygen molecule. Now, there are fifteen electrons in all. Therefore, electronic configuration is

$O_2^+ ; (\sigma\ 1s)^2\ (\sigma^*\ 1s)^2\ (\sigma 2s)^2\ (\sigma^*\ 2s)^2\ (\sigma 2p_z)^2$
$(\pi 2p_x)^2 = (\pi 2p_y)^2\ (\pi^*\ 2p_x)^1\ ;\ N_b = 10\ ;\ N_a = 5$

∴ **Bond order** $= \frac{1}{2}(N_b - N_a) = \frac{1}{2}(10 - 5) = 2.5.$

Due to the presence of one unpaired electron, O_2^+ ion is **paramagnetic**. Bond dissociation energy O_2^+ ion is 625 kJ mol^{-1} and bond length is 112 pm.

O_2^{2-}-Ion (Peroxide ion) : $O_2 + 2e$ Its electronic configuration is :

O_2^{2-} ion has two electrons more than O_2- molecule. Its electronic configuration is :

O_2^{2-} ; $(\sigma 1s)^2\ (\sigma^* 1s)^2\ (\sigma 2s)^2\ (\sigma^* 2s)^2\ (\sigma 2p_z)^2\ (\pi 2p_x)^2 = (\pi 2p_y)^2\ (\pi^* 2p_x)^2 = (\pi^* 2p_y)^2$

$N_b = 10$; $N_a = 8$

$\therefore$ **Bond order of O_2^{2-} ion is** $= \frac{1}{2}(10 - 8) = 1.$

The ion is diamagnetic due to the absence of unpaired electrons.

Relative stabilities of O_2, O_2^+, O_2^- and O_2^{2-}. As calculated above, the bond order of these species are 2, 2.5, 1.5 and 1 respectively. The bond dissociation energies are directly proportional to the bond order. Therefore, the bond dissociation energies of these species are in the order.

$$O_2^+ > O_2 > O_2^- > O_2^{2-}$$

The stabilities of species are directly proportional to their bond dissociation energies. Therefore, the order of stabilities is

$$O_2^+ > O_2 > O_2^- > O_2^{2-}$$

As bond length is inversely proportional to bond order, therefore, their bond lengths will be in the order:

$$O_2^{2-} > O_2^- > O_2 > O_2^+$$

(b) Molecular orbital treatment of heteroatomic diatomic molecules

(i) Carbon monoxide (CO).

$_6C = 1s^2\ 2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^0$; $\quad _8O = 1s^2\ 2s^2\ 2p_x^2\ 2p_x^1\ 2p_z^1$

CO-molecule is formed by the linear combination of atomic orbitals of carbon and oxygen atoms.

Number of electrons in C-atom = 6

Number of electrons in O-atom = 8

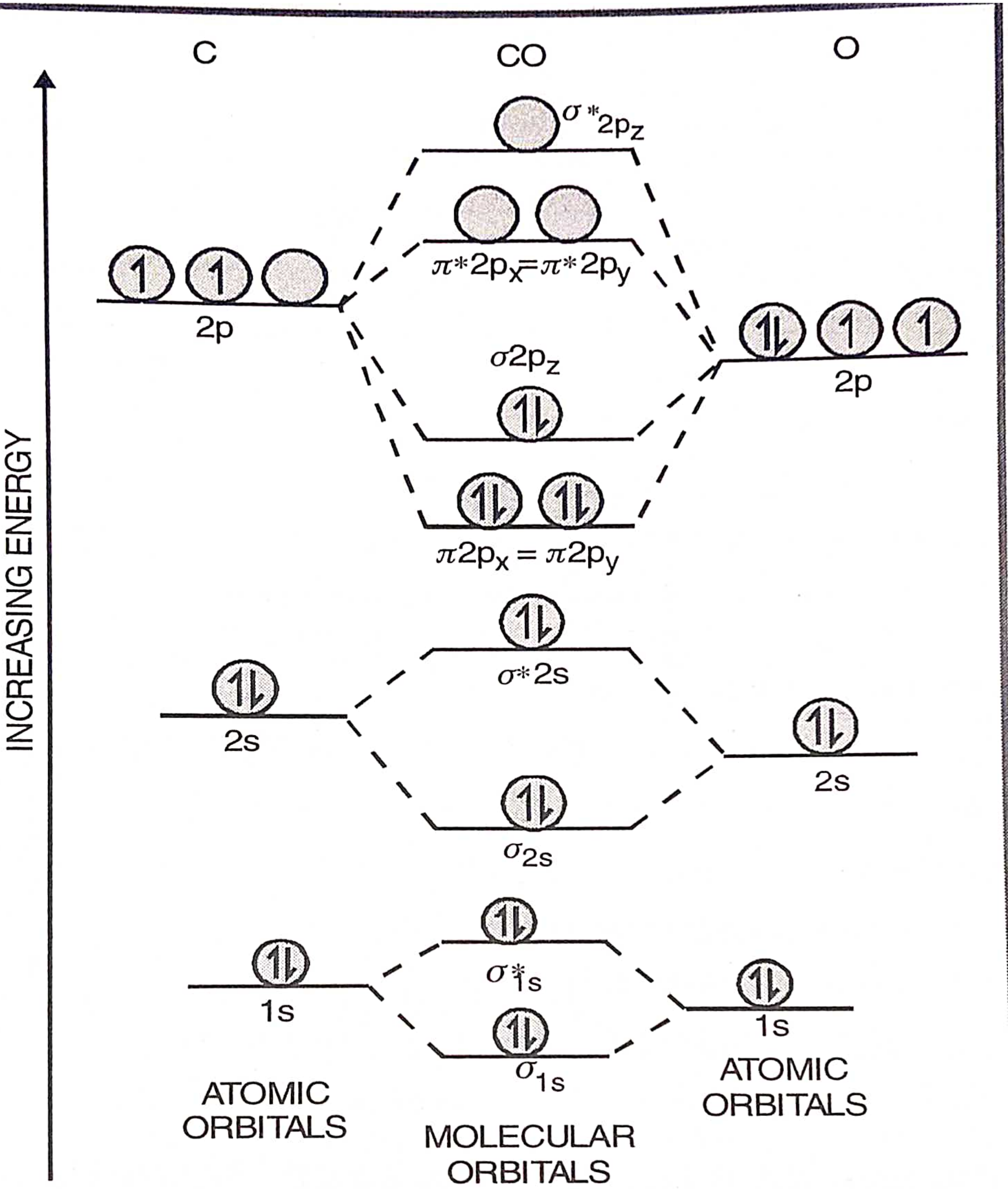
$\therefore$ Total number of electrons in CO = 6 + 8 = 14.

Since the total number of electrons in N_2-molecule is also 14 (At. No. of N = 7), the hetero- nuclear CO molecule may be regarded as perturbed N_2-molecule.

These 14 electrons are filled in various molecular orbitals with the help of *isoelectronic principle.* According to this principle:

"Isoelectronic molecular species (i.e., species having same number of atoms and same number of total valence electrons) have similar molecular orbitals and similar molecular structure."

Since CO (14 electrons) is isoelectronic with N_2 (14 electrons), the molecular orbital configuration of CO will be same as that of N_2.



C
CO
O
$\sigma^*_{2p_z}$
$\pi^*2p_x = \pi^*2p_y$
2p
$\sigma 2p_z$
2p
$\pi 2p_x = \pi 2p_y$
σ^*2s
2s
2s
σ_{2s}
σ^*_{1s}
1s
1s
σ_{1s}
ATOMIC ORBITALS
MOLECULAR ORBITALS
ATOMIC ORBITALS
INCREASING ENERGY

(than

(ii) Nitric oxide (NO)

$_7N = 1s^2\ 2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^1$; $\quad$ $_8O = 1s^2\ 2s^2\ 2p_x^2\ 2p_y^1\ 2p_z^1$

NO is formed by the linear combination of atomic orbitals of nitrogen and O-atoms.

Number of electrons in N-atom = 7

Number of electrons in O-atom = 8

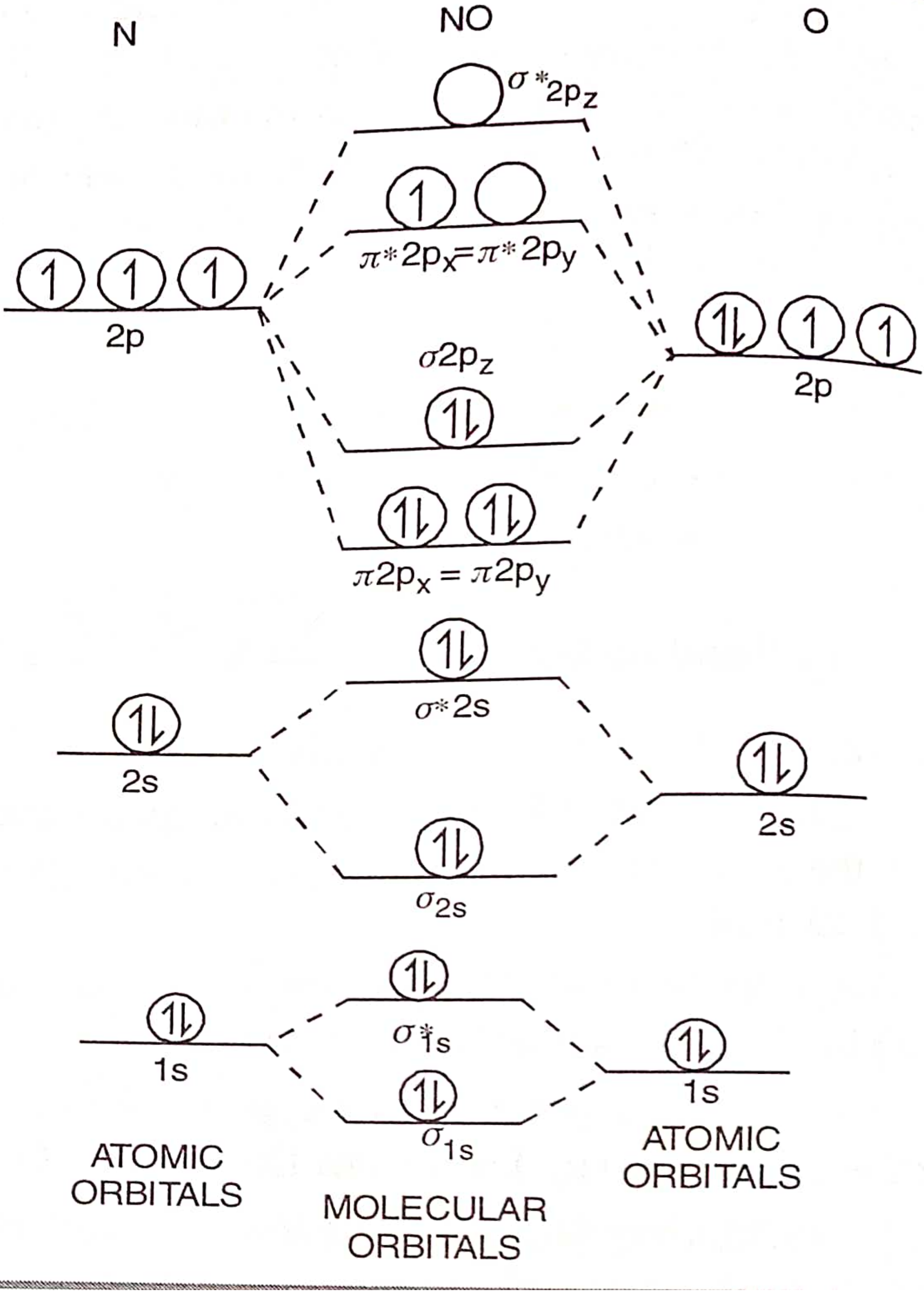
∴ Total number of electrons in NO = 7 + 8 = 15.

These 15 electrons are filled in various molecular orbitals in the increasing order of their energie (aufbau principle) and on the basis of Hund's rule and Pauli's exclusion principle.

(*i*) Molecular orbital energy level diagram of NO is shown in Fig. 2.52. The ground state of NO represented as :

$$(\sigma_{1s})^2\ (\sigma_{1s}^*)^2\ (\sigma_{2s})^2\ (\sigma_{2s}^*)^2\ (\pi_{2p_x})^2 = (\pi_{2p_y})^2\ (\sigma_{2p_z})^2\ (\pi_{2p_x}^*)^1 = (\pi_{2p_y}^*)^0$$

$$\textbf{Bond order} = \frac{N_b - N_a}{2} = \frac{10-5}{2} = 2.5$$


N
NO
O
σ*2p_z
π*2p_x=π*2p_y
2p
σ2p_z
2p
π2p_x = π2p_y
σ*2s
2s
2s
σ2s
σ*1s
1s
1s
σ1s
ATOMIC ORBITALS
MOLECULAR ORBITALS
ATOMIC ORBITALS