

# Chemical Bonding

## 1. OCTET RULE (LEWIS-KOSSEL RULE)

Noble gases have 8 electron in their outermost shell (complete octet) and outermost configuration is  $ns^2p^6$ . Every atom has a tendency to complete its octet by losing or gaining or by sharing electron.

### 1.1 Exceptions of Octet Rule

- (i) **Electron-Deficient Compounds** : Compounds having less than 8 electrons in the outermost shell of the central atom. e.g.  $BF_3$ ,  $BeCl_2$ ,  $AlCl_3$ .
- (ii) **Expansion of Octet** : The compounds having more than 8 electrons in the outermost shell of the central atom. e.g.  $PCl_5$ ,  $SF_6$
- (iii) **Transition Metal Ions** : Transition metal ions have 9 to 18 electrons in their outermost shell, e.g.  $Cr^{+3}$ ,  $Mn^{+2}$ ,  $Cu^+$
- (iv) H and Li atoms attain configuration like He by gaining and losing one electron, respectively, e.g.  $H^{-1}$ ,  $Li^{+1}$ .
- (v) **Odd Electron Bond** : Compounds having unpaired electron are also exceptions to the octet rule. The molecules having odd electrons are  $NO_2$ ,  $NO$ ,  $ClO_2$ ,  $O_2^{-1}$  etc.

Ex.1 Octet rule is not followed in :

[1]  $Ti^{+3}$                       [2]  $Na^{+1}$                       [3]  $Ca^{+2}$                       [4]  $K^{+1}$                       **Ans. [1]**

Sol.  $Ti^{+3}$  has 9 electron in its outermost shell.

Ex.2 Which of the following compounds has the central atom with incomplete octet ?

[1]  $NH_4^{+1}$                       [2]  $BCl_3$                       [3]  $CCl_4$                       [4]  $PCl_3$                       **Ans. [2]**

Sol. B has 6 electron in  $BCl_3$ .

Ex.3 An element forms cation by losing electron. The configuration of the cation may be like that of :

[1] inert gas                      [2] pseudo inert gas                      [3] inert pair                      [4] all above                      **Ans. [4]**

Sol. Inert gas – 8 electron in outermost shell. Pseudo inert gas – 18 electron in outermost shell.

### 1.2 Inert Pair Configuration

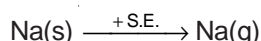
The heavy elements of IIIA, IV A and V A groups form cations having charge equal to group number and two less than group number, e.g.  $Tl^{+1}$ ,  $In^{+1}$ ,  $Sn^{+2}$ ,  $Pb^{+2}$ . In these elements due to more penetration power of s orbitals, the atom generally does not lose  $e^-$  present in ns orbital, so only np electrons are lost by the atom. This effect is called "inert pair effect".

## 2. IONIC BOND

- (i) Atoms get established by ion formation in formation of an ionic bond. One atom forms a cation by losing electrons and other forms anion by accepting electrons.
- (ii) The octets of the atoms are completed by transfer of electrons.
- (iii) Cations and anions are bonded by electrostatic force of attraction in ionic bond.
- (iv) Ionic bond is formed between metals (cations) and nonmetals (anions).
- (v) During the formation of an ionic bond, cation can attain one of the following configurations.
  - (a) **Inert Configuration** : I A and II A group metals (octet configuration)  $Na^{+1}$ ,  $Mg^{+2}$ ,  $K^{+1}$ ,  $Rb^{+1}$  attain  $s^2p^6$  inert configuration.
  - (b) **Pseudo Inert Configuration** : Metals of I B and II B groups –  $Cu^+$ ,  $Zn^{+2}$ ,  $Ag^{+1}$ ,  $Au^{+1}$ ,  $Cd^{+2}$ ,  $Hg^{+2}$ .
  - (c) Transition metals, e.g.  $Ti^{+3}$  (9),  $Ti^{+2}$  (10).

**(vi) Energies involved in ionic bond formation :**

(a) Sublimation Energy – The energy required to convert solid metal to gaseous state.



(b) Ionisation Energy – The energy required to remove an electron from the outermost shell of metal in gaseous state.

(c) Dissociation Energy – The energy required to convert the nonmetal molecule to atoms.



(d) Electron Affinity – The energy required during formation of an anion by addition of an electron to a nonmetal in gaseous state.

(e) Lattice Energy –

(i) The energy released during the formation of ionic bond.

(ii) Cations and anions form crystal lattice of ionic crystal in space by electrostatic force of attraction.

(iii) Lattice Energy  $\propto \frac{1}{r^+ + r^-}$

(f) Ionic compound is formed when the energy required (Sublimation energy + Ionisation energy + Dissociation energy) is less than energy released (Electron affinity + Lattice energy) So total energy change

$$-\Delta H = S + I + \frac{D}{2} - E - U$$

(Borne-Haber Equation)

**2.1 Factors Affecting Formation of Ionic Bond**

- (a) The sublimation energy and ionisation potential of a metal should be minimum so that it may easily form a cation.
- (b) The dissociation energy and electron affinity of a nonmetal should be high so that it may easily form an anion.
- (c) There should be a strong electrostatic force of attraction between cation and anion.
- (d) Metals have low ionisation potential and nonmetals have high electron affinity, so ionic bond is formed between metals and nonmetals.

**2.2 Characteristic of Ionic Compounds****(i) Solid and Crystalline Structure :**

Ionic compounds do not show molecular structure.

Ionic compounds have definite crystal structures.

CsCl has body centered cubic (BCC) structure.

**(ii) Melting and Boiling Point :**

Ionic compounds have high melting and boiling points.

**(iii) Hardness :**

Ionic compounds are solid with brittle nature.

**(iv) Conductivity :**

Ions are not free in solid state so ionic compounds are bad conductor of electric current in solid state but in solution and fused state electric current passes through and the ionic compound becomes good conductor of electricity

**(v) Solubility of Ionic Compounds :**

Ionic compounds are soluble in solvents which have high dielectric constant like water.

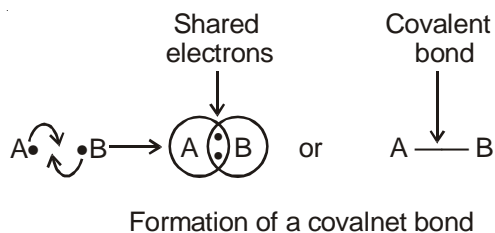
**(vi) Solvation of Hydration Energy :**

The energy released by the attraction of ions and solvent molecules is called solvation energy and when solvent is water this is called hydration energy.

$$\text{Solubility in water} = \text{Lattice energy} < \text{Hydration energy}$$

### 3. COVALENT BOND

A covalent bond is formed between two nonmetal atoms. e.g. in H–H, O=O and N≡N.



#### (a) Nonpolar Covalent Bonds :

Covalent bond between two identical atoms (e.g. H–H, O=O) electronegativity of both atom is same.

#### (b) Polar Covalent Bond :

When covalent bond is formed between two different atoms. e.g. HCl, HF

### 3.1 Characteristics of Covalent Compounds

#### 1. Physical State :

Covalent compounds generally occur in gaseous and liquid states, but sometimes in solid state also.

##### (a) Diamond :

- (i) In the structure of diamond, every carbon atom is attached to four other carbon atoms, tetrahedrally.
- (ii) Density of diamond is high.
- (iii) Every carbon atom is  $sp^3$  hybridised and forms four C–C  $\sigma$  bond by  $sp^3-sp^3$  overlapping
- (iv) Electrons are not free, so diamond is bad conductor of electricity.
- (v) Oxidation number of C in diamond is zero

##### (b) Graphite :

- (i) In the structure of graphite, every carbon atom is attached to three other carbon atoms forming hexagonal layers.
- (ii) Every carbon atom is  $sp^2$  hybridised and forms three  $\sigma$  bonds by  $sp^2-sp^2$  overlapping.
- (iii) Every carbon atom has one free electron. So graphite is a good conductor of electricity
- (iv) C–C bond length is 1.42 Å in plane.

#### 2. Boiling and Melting Points :

Melting and boiling points of covalent compounds are generally low due to weak van der Waals forces between molecules.

#### 3. Conductivity :

Covalent compounds are bad conductors of electricity.

**Ex.4**  $F_2$  and  $Cl_2$  are gases,  $Br_2$  is liquid and  $I_2$  is solid why ?

**Sol.** Intermolecular distance is high in gaseous state, low in solid state and intermediate in liquid state. When molecular weight increases, van der Waals forces also increase. So  $F_2$  and  $Cl_2$  are gases due to weak van der Waals forces and  $I_2$  is solid.

**Ex.5**  $\text{CHCl}_3$  is liquid but  $\text{CHI}_3$  is solid. Why ?

**Sol.** Due to increase in molecular weight, intermolecular force in  $\text{CHI}_3$  is greater than in  $\text{CHCl}_3$ .

**Ex.6**  $\text{CO}_2$  is gas but  $\text{SiO}_2$  is solid. Why ?

**Sol.**  $\text{CO}_2$  has only weak van der Waals forces, but in  $\text{SiO}_2$ , one silicon atom is surrounded by four oxygen atoms tetrahedrally forming macromolecular structure. So  $\text{SiO}_2$  is solid.

**Ex.7**  $\text{H}_2\text{O}$  is liquid but  $\text{H}_2\text{S}$  is a gas. Why ?

**Sol.**  $\text{H}_2\text{O}$  is liquid due to strong H-bonding.

**Ex.8**  $\text{NH}_3$  can be liquefied easily but  $\text{PH}_3$  is not. Why ?

**Sol.** H-bonding present in  $\text{NH}_3$ , while  $\text{PH}_3$  is nonpolar due to same value of electronegativity of P and H.

#### 4. DIPOLE MOMENT

Polarity of bond is measured by dipole moment. The product of charge (e) and internuclear distance (d) between two poles of polar molecule is called dipole moment ( $\mu$ ). The unit of dipole moment is Debye (D).  $\mu = e \cdot d$ .

$$\text{Percentage of ionic character} = \frac{\mu(\text{obs.})}{\mu(\text{cal.})} \times 100 \quad [1\text{D} = 10^{-18} \text{ e.s.u cm}]$$

(i) Dipole moment of nonpolar compounds is zero.

(ii) When the electronegativity difference of atoms in compounds increases dipole moment also increases.

(iii) If the structure of a compound is symmetric like linear, trigonal planar & Tetrahedral the dipole moment will be zero. e.g.  $\text{BF}_3$ ,  $\text{BCl}_3$ ,  $\text{CF}_4$ ,  $\text{CCl}_4$ ,  $\text{CH}_4$  etc.

(iv) Structure of  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ ,  $\text{CH}_3\text{F}$  is tetrahedral, but due to different bonds, dipole moment will not be zero.

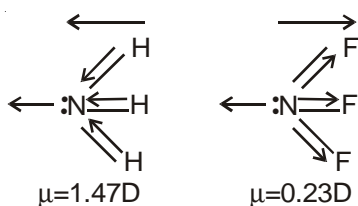
**Ex.9** What will be the dipole moment of HCl if  $d = 1.34 \text{ \AA}$  and charge =  $4.8 \times 10^{-10} \text{ esu}$  ? Calculate ionic character of the bond when observed value of  $\mu$  is 1.08D.

**Sol.**  $\mu_{(\text{cal.})} = e \cdot d$   
 $= 4.8 \times 10^{-10} \times 1.34 \times 10^{-8}$   
 $= 6.4 \times 10^{-18} \text{ esu cm}$

$$\text{Percentage of ionic character} = \frac{1.08 \times 10^{-18}}{6.40 \times 10^{-18}} \times 100 = 16.88\%$$

**Ex.10** Dipole moment of  $\text{NH}_3$  is greater than that of  $\text{NF}_3$ .

**Sol.** N-H bond moment and lone pair moment in  $\text{NH}_3$  add up because they are in same direction. In  $\text{NF}_3$  ionisation lone pair moment and N-F bond moment are in opposite direction. So dipole moment will decrease.



Dipole Moments of some Compounds

**Ex.11** Which of the following compounds should have zero dipole moment.

[1] CO                      [2] CCl<sub>4</sub>                      [3] NH<sub>3</sub>                      [4] CH<sub>3</sub>Cl                      **Ans. [2]**

**Sol.** Tetrahedral geometry of CCl<sub>4</sub> in which four C–Cl bond moments balance each other.

**Ex.12** Which of the following compounds should have higher dipole moment than the remaining three?

[1] HF                      [2] H<sub>2</sub>O                      [3] NH<sub>3</sub>                      [4] NF<sub>3</sub>                      **Ans. [2]**

**Sol.** Higher dipole moment of H<sub>2</sub>O is due to H-bonding.

## 5. BOND PAIR AND LONE PAIR

(i) In covalent compounds, the number of bond pairs is equal to the number of shared pairs of electron.

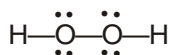
$$\text{Number of bond pairs} = \text{Number of bonds}$$

(ii) The electron pair, which does not participate in bond formation, is called lone pair.

(iii) :N≡N: (N<sub>2</sub>) 2 lone pairs and 3 bond pairs.

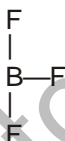
(iv) : $\ddot{\text{C}}\text{I}$  –  $\ddot{\text{C}}\text{I}$ : (Cl<sub>2</sub>) 6 lone pairs and 1 bond pairs.

**Ex.13** What are the numbers of lone pairs and bond pairs in H<sub>2</sub>O<sub>2</sub> molecule ?



**Sol.** Lone pair = 4, Bond pair = 3

**Ex.14** What are the numbers of lone pairs and bond pairs on B in BF<sub>3</sub> ?

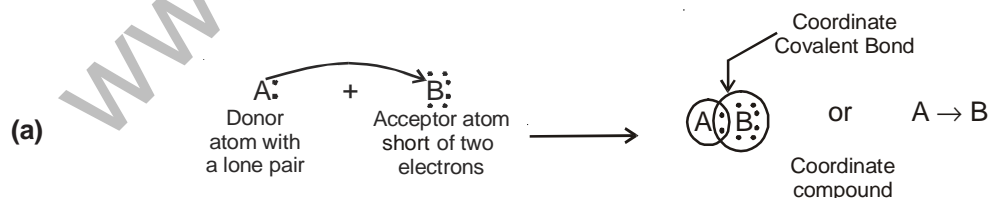


**Sol.** Lone Pair = 0, Bond Pair = 3

## 6. COORDINATE BOND OR DATIVE BOND OR COORDINATE COVALENT BOND

(i) Coordinate bond is formed by unequal sharing of electron pair between two atoms, one of which, called the donor atom, provides the electron pair and the other atom, called the acceptor atom, receives that electron pair.

(ii) The donor should have complete octet with a lone pair of electrons and acceptor atom should have incomplete octet and a vacant orbital to accept the electron pair.



It is also known as **Dative Bond**, according to Scientist, **Menzie**.

(iii) Formation of covalent bond is essential before formation of coordinate bond.

(iv) This bond is different from a covalent bond, in the latter one electron provided by each of the bonding atoms.

(v) Coordinate bond is also different from ionic bond because electrons are not completely transferred.

(vi) In this bond, electrons are donated only in the form of pairs.

(vii) Electron pair is provided by only one atom and shared equally by both the atoms. So according to Sugden it is a polar bond.

(viii) Once a coordinate bond is formed, there remains no difference between the coordinate and covalent bonds. So the property of coordinate compounds are similar to those of covalent compounds.

Ex.15 Which of the following compounds has coordinate bond ?

[1] Methyl cyanide      [2] Methyl isocyanate      [3] Methyl cyanate      [4] None of these      **Ans. [3]**

Sol.  $\text{CH}_3\text{C}\equiv\text{N}\rightarrow\text{O}$

**Structures of Some Compounds**

S. No.	Name of the Compound	Formula	Structure
1.	Sulphur dioxide	$\text{SO}_2$	$\begin{array}{c} \text{S}=\text{O} \\ \downarrow \\ \text{O} \end{array}$
2.	Sulphur trioxide	$\text{SO}_3$	$\begin{array}{c} \text{O} \leftarrow \text{S} \rightarrow \text{O} \\    \\ \text{O} \end{array}$
3.	Hydronium ion	$\text{H}_3\text{O}^+$	$\left[ \begin{array}{c} \text{H}-\text{O}-\text{H} \\ \downarrow \\ \text{H} \end{array} \right]^+$
4.	Ammonium ion	$\text{NH}_4^+$	$\left[ \begin{array}{c} \text{H} \\   \\ \text{H}-\text{N}-\text{H} \\ \downarrow \\ \text{H} \end{array} \right]^+$
5.	Sulphuric acid	$\text{H}_2\text{SO}_4$	$\begin{array}{c} \text{O} \\ \uparrow \\ \text{H}-\text{O}-\text{S}-\text{O}-\text{H} \\ \downarrow \\ \text{O} \end{array}$
6.	Nitric acid	$\text{HNO}_3$	$\begin{array}{c} \text{H}-\text{O}-\text{N}=\text{O} \\ \downarrow \\ \text{O} \end{array}$
7.	Carbon monoxide	$\text{CO}$	$\text{C}\equiv\text{O}$
8.	Sulphate ion	$\text{SO}_4^{2-}$	$\begin{array}{c} \text{O} \\ \uparrow \\ \text{O}^- - \text{S} - \text{O}^- \\ \downarrow \\ \text{O} \end{array}$
9.	Chlorate ion	$\text{ClO}_3^-$	$\begin{array}{c} \text{O} \\ \uparrow \\ \text{O} - \text{Cl} \rightarrow \text{O} \\ \downarrow \\ \text{O} \end{array}$
10.	Perchloric acid	$\text{HClO}_4$	$\begin{array}{c} \text{O} \\ \uparrow \\ \text{HO} - \text{Cl} \rightarrow \text{O} \\ \downarrow \\ \text{O} \end{array}$
11.	Carbonate ion	$\text{CO}_3^{2-}$	$\begin{array}{c} \text{O}^- - \text{C} - \text{O}^- \\    \\ \text{O} \end{array}$
12.	Carbonic acid	$\text{H}_2\text{CO}_3$	$\begin{array}{c} \text{H}-\text{O}-\text{C}-\text{O}-\text{H} \\    \\ \text{O} \end{array}$
13.	Phosphate ion	$\text{PO}_4^{3-}$	$\begin{array}{c} \text{O} \\ \uparrow \\ \text{O}^- - \text{P} - \text{O}^- \\   \\ \text{O}^- \end{array}$

S. No.	Name of the Compound	Formula	Structure
14.	Orthophosphoric acid	$\text{H}_3\text{PO}_4$	$\begin{array}{c} \text{O} \\ \uparrow \\ \text{HO}-\text{P}-\text{O}-\text{H} \\   \\ \text{O}-\text{H} \end{array}$
15.	Sulphuric chloride	$\text{SO}_2\text{Cl}_2$	$\begin{array}{c} \text{O} \\ \uparrow \\ \text{Cl}-\text{S}-\text{Cl} \\ \downarrow \\ \text{O} \end{array}$
16.	Hypophosphorous acid	$\text{H}_3\text{PO}_2$	$\begin{array}{c} \text{H} \\   \\ \text{H}-\text{O}-\text{P} \rightarrow \text{O} \\   \\ \text{H} \end{array}$
17.	Orthophosphorous acid	$\text{H}_3\text{PO}_3$	$\begin{array}{c} \text{O} \\ \uparrow \\ \text{H}-\text{P}-\text{O}-\text{H} \\   \\ \text{O}-\text{H} \end{array}$
18.	Thiosulphate ion	$\text{S}_2\text{O}_3^{2-}$	$\left[ \begin{array}{c} \text{O} \\ \uparrow \\ \text{O} - \text{S} - \text{O} \\ \downarrow \\ \text{S} \end{array} \right]^{2-}$
19.	Dicromate ion	$\text{Cr}_2\text{O}_7^{2-}$	$\begin{array}{c} \text{O} \quad \text{O} \\ \uparrow \quad \uparrow \\ \text{O} - \text{Cr} - \text{O} - \text{Cr} - \text{O} \\ \downarrow \quad \downarrow \\ \text{O} \quad \text{O} \end{array}$
20.	Permanganate ion	$\text{MnO}_4^-$	$\begin{array}{c} \text{O} \\ \uparrow \\ \text{O} - \text{Mn} - \text{O} \\ \downarrow \\ \text{O} \end{array}$
21.	Dichloro septoxide	$\text{Cl}_2\text{O}_7$	$\begin{array}{c} \text{O} \quad \text{O} \\ \uparrow \quad \uparrow \\ \text{O} \leftarrow \text{Cl} - \text{O} - \text{Cl} \rightarrow \text{O} \\ \downarrow \quad \downarrow \\ \text{O} \quad \text{O} \end{array}$
22.	Nitrogen pentoxide	$\text{N}_2\text{O}_5$	$\begin{array}{c} \text{O} \leftarrow \text{N} - \text{P} - \text{N} \rightarrow \text{O} \\    \quad    \\ \text{O} \quad \text{O} \end{array}$
23.	Nitrogen trioxide	$\text{N}_2\text{O}_3$	$\begin{array}{c} \text{O} \\ \uparrow \\ \text{O}=\text{N}-\text{N}=\text{O} \end{array}$
24.	Nitrus oxide	$\text{N}_2\text{O}$	$\text{N}\equiv\text{N}\rightarrow\text{O}$



S. No.	Name of the Compound	Formula	Structure
25.	Nitromethane	CH <sub>3</sub> NO <sub>2</sub>	$\begin{array}{c} \text{CH}_3-\text{N}=\text{O} \\ \downarrow \\ \text{O} \end{array}$
26.	Methyl nitrite	CH <sub>3</sub> NO <sub>2</sub>	CH <sub>3</sub> -O-N=O
27.	Methyl isocyanide	CH <sub>3</sub> NC	$\begin{array}{c} \text{H} \\   \\ \text{H}-\text{C}-\text{N} \equiv \text{C} \\   \\ \text{H} \end{array}$
28.	Ozone	O <sub>3</sub>	$\begin{array}{c} \text{O} \\ // \quad \backslash \\ \text{O} \quad \text{O} \end{array}$
29.	Methyl cyanide	CH <sub>3</sub> CN	$\begin{array}{c} \text{H} \\   \\ \text{H}-\text{C}-\text{C} \equiv \text{N} \\   \\ \text{H} \end{array}$

S. No.	Name of the Compound	Formula	Structure
30.	Methyl cyanate	CH <sub>3</sub> CNO	$\begin{array}{c} \text{H} \\   \\ \text{H}-\text{C}-\text{C} \equiv \text{N} \rightarrow \text{O} \\   \\ \text{H} \end{array}$
31.	Methyl isocyanate	CH <sub>3</sub> NCO	CH <sub>3</sub> -N=C=O
32.	Fluoroborate ion	BF <sub>4</sub> <sup>-1</sup>	$\left[ \begin{array}{c} \text{F} \\   \\ \text{F}-\text{B} \leftarrow \text{F} \\   \\ \text{F} \end{array} \right]^{-1}$
33.	Pyrophosphoric acid	H <sub>4</sub> P <sub>2</sub> O <sub>7</sub>	$\begin{array}{c} \text{O} \quad \text{O} \\ \uparrow \quad \uparrow \\ \text{H}-\text{O}-\text{P}-\text{O}-\text{P}-\text{O}-\text{H} \\   \quad   \\ \text{O} \quad \text{O} \\   \quad   \\ \text{H} \quad \text{H} \end{array}$
34.	Anhydrous aluminium chloride	Diameric Al <sub>2</sub> Cl <sub>6</sub> or Halogen-bridge compound	

## 6.1 Characteristics of Coordinate Compounds

- (i) These compounds show partial ionic character due to polar nature.
- (ii) Melting and boiling points of these compounds are less than those of ionic compounds and more than those of covalent compounds.
- (iii) **Solubility** : These are partially soluble in water (polar solvent) and soluble in nonpolar solvents.
- (iv) **Conductivity** : Coordinate compounds are bad conductor of electricity due to absence of ions.
- (v) **Stability** : These are stable due to polar nature. When bonding molecules are independently stable, the coordinate bond is less stable, e.g. in H<sub>3</sub>N→BF<sub>3</sub> molecule, the coordinate bond is less stable because NH<sub>3</sub> and BF<sub>3</sub> are themselves stable.

## 6.2 Compounds Having Ionic, Covalent and Coordinate Bonds

Some compounds have all the three types of bonds, i.e. ionic, covalent and coordinate bond, e.g.

- (i) NH<sub>4</sub>Cl – Ionic bond between NH<sub>4</sub><sup>+</sup> and Cl<sup>-</sup> and covalent bonds and a coordinate bond are present in NH<sub>4</sub><sup>+</sup>.

## 7. IONIC CHARACTER IN COVALENT COMPOUNDS

- (i) When electronegativity difference of two atoms is less than 0.8, the covalent bond is nonpolar, e.g. PH<sub>3</sub>.
- (ii) When electronegativity difference of atoms is 0.1 to 0.8, the bond between them is nonpolar covalent bond. When electronegativity difference of atoms is 0.8 to 1.6, the bond between them is polar covalent bond. Then electronegativity difference is 1.7 to 3.2, the bond is ionic.

$$\text{Ionic character} \propto \text{Electronegativity difference of bonded atoms}$$

- (iii) Pauling used dipole moment for depicting percentage of polarity and ionic character of the bond. According to Pauling, a bond can never be 100% ionic.
- (iv) When electronegativity difference between two atoms is 2.1, there is 50% ionic character in the bond.

- (v) When electronegativity difference is zero (identical atoms), the bond will be 100% covalent.

According to Haney and Smith, the percentage of ionic character of a polar covalent bond can be calculated with help of the following expression.

$$\% \text{ Ionic character} = (0.16\Delta + 0.035\Delta^2) \times 100$$

Where  $\Delta$  = Electronegativity difference between bonded atoms.

- Ex.16** Atomic number of A, B and C are Z, Z + 1 and Z + 2, respectively, and C is an alkali metal. What should be the nature of bond between A and C ?

[1] Ionic                      [2] Coordinate                      [3] Covalent                      [4] Hydrogen bond                      **Ans. [1]**

- Sol.** (Z + 2) stands for alkali metal, (Z + 1) for inert gas and Z for halogen. Since A is halogen and C is alkali metal, the nature of bond will be ionic.

- Ex.17** Three electrons are present in the outermost shell of an element A and six electrons in that of B. What compound will be formed by A and B ?

[1]  $A_2B_3$                       [2]  $AB_2$                       [3]  $A_6B_6$                       [4] All of the above                      **Ans. [1]**

- Sol.** A has 3 electrons in outermost shell, like Al. B has 6 electrons in outermost shell, like O, their compound will be  $Al_2O_3$ , i.e.  $A_2B_3$ .

- Ex.18** Compound having dative and covalent bond, is :

[1]  $SO_2$                       [2]  $NH_4Cl$                       [3]  $CuSO_4 \cdot 5H_2O$                       [4]  $AgCl$                       **Ans. [1]**

- Sol.** All the three types of bonds are present in  $NH_4Cl$  and  $CuSO_4$ , ionic bond in  $AgCl$  and both dative and covalent bonds in  $SO_2$ .

- Ex.19** Compound formed by the elements having atomic number 6 and 16, will be :

[1] Ionic                      [2] Covalent                      [3] Coordinate                      [4] Hydrogen bonded                      **Ans.[2]**

- Sol.** Atomic number 6 = Carbon ; Atomic number 16 = Sulphur  
The compound will be  $CS_2$  (covalent)

- Ex.20** Diamond and graphite are :

[1] isotone                      [2] isomers                      [3] isotope                      [4] allotropes                      **Ans.[4]**

- Sol.** Diamond and graphite are allotropic forms of carbon.

- Ex.21** Which of the following compounds has ionic and covalent bonds ?

[1]  $NaCN$                       [2]  $CO_2$                       [3]  $NaCl$                       [4]  $N_2$

- Sol.**  $Na^+ C \equiv N^-$

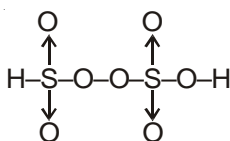
- Ex.22** Inorganic graphite is :

[1] boron nitrate                      [2] boron nitride (BN)                      [3] boron carbonate                      [4] None of the above                      **Ans. [2]**

- Ex.23** In disulphuric acid ( $H_2S_2O_7$ ), the number of covalent bonds and coordinate bonds, respectively, are

[1] 6 and 4                      [2] 6 and 6                      [3] 4 and 4                      [4] 4 and 6                      **Ans. [1]**

- Sol.** Structure of  $H_2S_2O_7$  is





**Ex.24** When electronegativity difference of B and Cl is 1.0, the % ionic character in the bond will be :

- [1] 10%                      [2] 19.5%                      [3] 30%                      [4] 45.5%

**Ans. [2]**

**Sol.**  $\Delta = 1.0$

$$\begin{aligned} \text{\% ionic character} &= (0.16 \times 1 + 0.035 \times 1^2) \times 100 \\ &= 0.195 \times 100 = 19.5\% \end{aligned}$$

**Ex.25** What should be the percentage ionic character in CsF when electronegativity difference is 3.3 ?

- [1] 90.9%                      [2] 0.09%                      [3] 93.3%                      [4] 95.7%

**Ans. [1]**

**Sol.** % ionic character

$$\begin{aligned} &= (0.16 \times 3.3 + 0.035 \times 3.3^2) \times 100 \\ &= 90.9\% \end{aligned}$$

**Ex.26** What is the increasing order of ionic character in  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{S}$  and  $\text{H}_2\text{Se}$  ?

**Sol.** Electronegativity difference is maximum in H and O. So  $\text{H}_2\text{Se} < \text{H}_2\text{S} < \text{H}_2\text{O}$

**Ex.27** What is the increasing order of ionic character in  $\text{OF}_2$  and  $\text{Cl}_2\text{O}$  ?

**Sol.** Electronegativity difference in F–O is greater than in O–Cl.  $\therefore \text{Cl}_2\text{O} < \text{OF}_2$

## 8. COVALENT CHARACTER IN IONIC COMPOUNDS (FAJAN'S RULE)

Some ionic compounds show that covalent character by polarization of anion

(i) **Size of Cation** : Size of cation must be small

$$\text{Covalent character} \propto \frac{1}{\text{Size of cation}}$$

$$\text{ionic character} \propto \text{Size of cation}$$

(ii) **Size of Anion** : Size of anion must be large

$$\text{Covalent character} \propto \text{Size of anion}$$

$$\text{Ionic character} \propto \frac{1}{\text{Size of anion}}$$

(iii) **Charge on Cation and Anion** :

$$\text{Covalent character} \propto \text{Charge on cation and anion}$$

(iv) **Inert and Pseudo Inert Structures** :

Configuration of cations must be equal to pseudo inert type  $[\text{ns}^0 (\text{n} - 1) \text{d}^{10}]$  e.g.  $\text{Cu}^+$ ,  $\text{Ag}^+$ ,  $\text{Au}^+$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Pb}^{4+}$  etc.

**Ex.28**  $\text{AgCl}$  is white,  $\text{AgBr}$  is yellow and  $\text{AgI}$  is deep yellow, why ?

**Sol.**  $\text{I}^-$  is largest, so polarization of  $\text{I}^-$  by  $\text{Ag}^+$  is maximum and the shared electrons are easily transferred to higher energy level in visible light. So  $\text{AgI}$  is deep yellow. But in chloride, electrons are transferred easily. So  $\text{AgCl}$  is colourless similarly.

(i)  $\text{SnCl}_2$  is white but  $\text{SnI}_2$  is yellow.

(ii)  $\text{PbCl}_2$  is white but  $\text{PbI}_2$  is yellow.

(iii)  $\text{HgCl}_2$  is white but  $\text{HgI}_2$  is red.

(iv)  $\text{SbCl}_3$  is white but  $\text{SbI}_3$  is black.

## 8.1 Applications of Fajjans Rule

Due to polarization of anion compounds gives a specific colour.

### 8.1.1 Ionic Potential

- (i) It is represented by  $\phi$  and is only for cation.

$$\text{Ionic potential} = \frac{\text{Charge on cation}}{\text{Size of cation}}$$

- (ii) When the size of cation is small and the charge is high, the value of  $\phi$  is high and the polarizing power of cation is also high.
- (iii) In a period, radius decreases but charge increases. So  $\phi$  increases and the covalent character of the bond increases.



### 8.1.2 Application of Ionic Potential

#### (a) Nature of Bond :

- (i) When  $\sqrt{\phi} < 2.2$ , the bond is ionic

Example – NaCl, KCl, RbCl, BaCl<sub>2</sub>, CaCl<sub>2</sub>, SnCl<sub>2</sub>, etc.

- (ii) If  $\sqrt{\phi} > 2.2$ , the bond is covalent.

Example – LiCl, BeCl<sub>2</sub>, BCl<sub>3</sub>, etc,

Covalent character  $\propto \sqrt{\phi}$

#### (b) Acidic and Basic Nature of Metal Oxides :

- (i) If  $\sqrt{\phi} < 2.2$ , the oxide is basic.

Example – Oxides of groups I A and II A.

$$\text{Basic character of oxides} \propto \frac{1}{\sqrt{\phi}}$$

- (ii) If  $\sqrt{\phi} = 2.2$  to 3.2, the oxide is amphoteric.

Example – Oxides of groups III A and IV A

- (iii) If  $\sqrt{\phi} > 3.2$  then oxide will be acidic

Example – Oxides of V A, VI A and VII A

#### (c) Boiling and Melting Points of Compounds :

In a group,  $\sqrt{\phi}$  decreases and the ionic character also increases. Therefore, melting points and boiling points increase.

#### (d) Nature of Metal Halides :

When  $\sqrt{\phi}$  of metal  $< 2.2$ , the ionic character and conductivity increase and when  $\sqrt{\phi} > 2.2$ , the covalent character increases and conductivity decreases.

$$\text{Formation of complex ion} \propto \sqrt{\phi}$$

**Ex.29** Which of the following compounds has minimum melting point ?

[1] PbCl<sub>2</sub>

[2] SnCl<sub>2</sub>

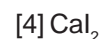
[3] NaCl

[4] SnF<sub>4</sub>

**Ans. [4]**

**Sol.** Covalent character  $\propto$  Charge on cation

**Ex.30** Which of the following compounds has maximum melting point ?



Ans. [1]

**Sol.**  $\text{F}^-$  is smallest, so  $\text{CaF}_2$  is most ionic. Thus, melting point and boiling point are maximum.

$$\text{Ionic character} \propto \frac{1}{\text{Size of anion}}$$

**Ex.31** The order of ionic size is  $\text{Na}^+ > \text{Mg}^{+2}$  and  $\text{S}^{-2} > \text{Cl}^-$ . Which of these compounds is least soluble in polar solvents ?



Ans. [1]

**Sol.**  $\text{Mg}^{+2}$  (small cation) and  $\text{S}^{-2}$  (large anion), therefore,  $\text{MgS}$  is covalent, so least soluble in polar solvents.

**Ex.32** Melting point of  $\text{SnCl}_2$  is  $606^\circ$  while melting point of  $\text{SnCl}_4$  is  $114^\circ\text{C}$ . Why ?

**Sol.**  $\text{SnCl}_4$  is covalent due to small size of  $\text{Sn}^{+4}$ .

**Ex.33** Which of the following compounds has least ionic character ?



Ans. [4]

**Sol.**  $\text{Hg}^{+2}$  is pseudo inert ion, but others are inert ions.

## 9. BOND LENGTH

The distance between nuclei of two bonded atoms is called bond length.

Factors effecting Bond Length

### 1. Radius of Bonded Atoms :

Bond length increases with increase in radii of the bonded atoms.



### 2. Difference Between Electronegativity of Two Bonded Atoms :

Bond length can be determined by the relation given by **Shoemaker and Stevenson**.

$$d_{\text{A-B}} = r_{\text{A}} + r_{\text{B}} - 0.09 (\Delta)$$

$$d_{\text{A-B}} = \text{Bond length}$$

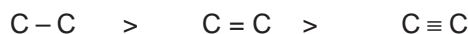
$$r_{\text{A}} = \text{Radius of A}$$

$$r_{\text{B}} = \text{Radius of B}$$

$$\Delta = \text{Difference in electronegativity of A and B.}$$

### 3. Bond Order :

Bond length of single bond is greater than that of the double bond and bond length of double bond is greater than that of triple bond.



### 4. Hybridization :

When s character in hybrid orbitals increases, bond length decreases, because s orbital is attracted by the nucleus with greater force.

$$\text{Bond length} \propto \frac{1}{\text{s character in hybrid orbital}}$$

$$\text{or bond length} \propto \text{p character in hybrid orbital}$$

**Ex.34** Which of the following statements is not true ?

[1] N–N bond length in  $N_2$  is less than in  $NH_2-NH_2$

[2] O–O bond length in  $O_3$  is less than in  $H_2O_2$

[3] Bond length in H–Cl is greater than in H–F

[4] Bond length in  $H_2S$  is greater than in  $H_2Se$

**Ans. [4]**

**Sol.** Electronegativity of S is greater than that of Se. So bond length in  $H_2S$  is less than bond length in  $H_2Se$ .

**Ex.35** Correct order of bond length of N–H in  $NH_3$ , and bond length of N–F in  $NF_3$  is :

[1]  $N-H = N-F$

[2]  $N-F < N-H$

[3]  $N-F > N-H$

[4] None of these

**Ans. [3]**

**Sol.** The electronegativity difference of N–F is less than that in N–H. So N–H bond is more polar.

## 10. BOND ANGLE

Bond angle between two adjacent bonds in a molecule is called bond angle.

Factors effecting Bond Angle

### 1. Type of Hybridization :

Bond angle depends on hybridization of an atom. Increasing order of bond angle is as follows :



Hybridization	$sp^3$	$sp^2$	$sp$
Bond angle	$109^\circ 28'$	$120^\circ$	$180^\circ$

$$\text{Bond angle} \propto \text{s-character in hybrid orbitals}$$

$$\text{Bond angle} \propto \frac{1}{\text{p-character in hybrid orbitals}}$$

### 2. Lone Pair of Electrons :

Bond angle decreases with increase in the number of lone pairs on the central atom.

$$\text{Bond angle} \propto \frac{1}{\text{Number of lone pairs}}$$

### 3. Electronegativity of Central Atom :

Bond angle will be high if the electronegativity value of the central atom is high.

$$\text{Bond angle} \propto \text{Electronegativity of central atom}$$

Molecule	$H_2O$	$H_2S$	$H_2Se$
Bond angle	$105^\circ$	$92^\circ$	$37.5^\circ$

## 11. BOND ENERGY

The energy released during formation of one mole gaseous substance from two neutral gaseous species is called bond energy of the bond formed.

### (a) Dissociation Energy :

The energy required to dissociate the bond into two neutral atoms is called dissociation energy.

### (b) Bond Energy :

More than one bond is present in a polyatomic molecule. So, the average of bond dissociation energies of different bonds is called bond energy.

### 11.1 Factors Affecting Bond Energy

#### (1) Atomic Radius :

Bond energy decreases with increase in atomic size because overlapping decreases.



$$\text{Bond energy} \propto \frac{1}{\text{atomic radius}}$$

#### (2) Bond length :

Bond energy increase with decrease in bond length because of more effective orbital overlap.



$$\text{Bond energy} \propto \frac{1}{\text{Bond length}}$$

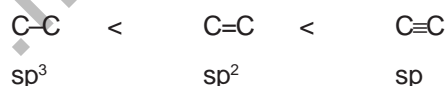
#### (3) Polarity of the Bond :

Bond energy increases with polarity of bond and polarity depends on difference in electronegativity.



#### (4) Hybridization :

Bond energy increases with increase in s-character or decrease in p-character in hybrid orbital.

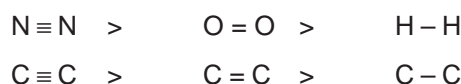


$$\text{Bond energy} \propto \text{s-character in hybrid orbital}$$

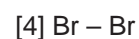
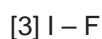
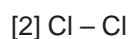
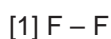
$$\text{Bond energy} \propto \frac{1}{\text{p-character in hybrid orbital}}$$

#### (5) Bond Order :

Bond energy increases with bond order.



**Ex.36** Highest bond energy will be.



**Ans. [2]**

**Sol.** Due to small size of F atoms, electron-electron (l.p.) repulsion will be effective, so bond energy of F<sub>2</sub> will be less than Cl<sub>2</sub>.

**Ex.37**  $\text{NF}_3$  is more stable than  $\text{NCl}_3$ . Why ?

**Sol.**  $\text{NF}_3$  is more polar than  $\text{NCl}_3$ . So bond energy of will be higher.

**Ex.38** The bond energy of  $\text{I}_2$  and  $\text{Cl}_2$  is 150.6 and 247.8 kJ./mole. Calculate the bond energy of  $\text{ICl}$  bond.

**Sol.**  $\text{I}_2 = 150.6$                        $\text{Cl}_2 = 247.8$

$\text{I} = 75.3$                                  $\text{Cl} = 123.9$

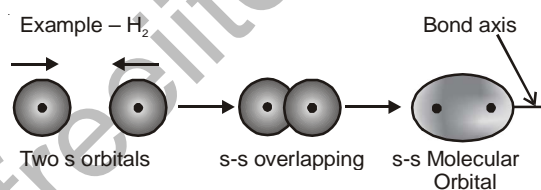
$\text{ICl} = 75.3 + 123.9 = 199.2 \text{ KJ/mole.}$

## 12. OVERLAPPING

- (i) Overlapping does not take place in ionic bond, only takes place in covalent bond.
- (ii) The orbitals of unpaired electrons overlap in the formation of covalent bond.
- (iii) When overlapping is coaxial, a  $\sigma$  bond is formed and when overlapping is collateral, a  $\pi$  bond is formed.
- (iv) A  $\sigma$  bond is stronger than a  $\pi$  bond.
- (v) A  $\pi$  bond is never formed along as it is very weak. It is formed after a  $\sigma$  bond is formed.
- (vi) s-Orbital always forms  $\sigma$  bond.

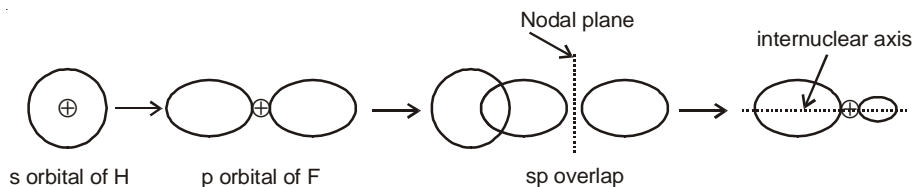
### 12.1 Types of Overlapping

- (i) **s-s Overlapping** – When two s orbitals of two atoms each having an unpaired electron, participate in overlapping, it is called s-s overlapping.



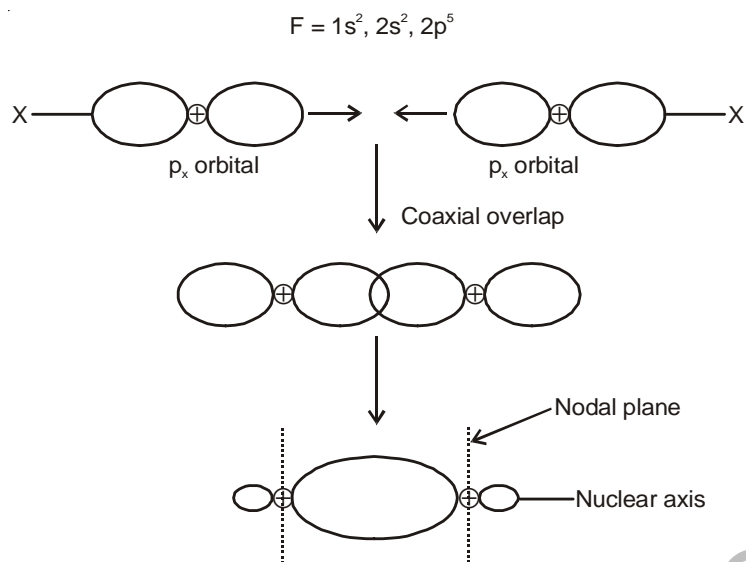
Formation of  $\text{H}_2$  by s-s overlapping

- (ii) **s-p Overlapping** – When s orbital of an atom and p orbital of the other atom, each having one unpaired electron, participate in overlapping, a sausage-shaped  $\sigma$  molecular orbital is formed.



- (iii) **p-p Overlapping** – Two p orbitals can form either a  $\sigma$  bond or a  $\pi$  bond by different type of overlapping. When overlapping of p orbital is coaxial, a  $\sigma$  bond is formed and when it is collateral, a  $\pi$  bond is formed.





1. p-p (coaxial) > s-p > s-s
2. p-p (coaxial) > p-p- (collateral)

**Ex.39** Four bonds are never formed between two atoms. Why ?

**Sol.** There are three axes (x, y and z) perpendicular to each other. A maximum of two  $\pi$  bonds can be formed by collateral overlapping and one  $\sigma$  bond is formed by coaxial overlapping. Thus, highest bond order between two atoms can be three and never four.

**Ex.40** p-p Overlapping is not possible in :

- [1]  $Cl_2$                       [2]  $O_2$                       [3]  $N_2$                       [4]  $H_2$                       **Ans. [4]**

**Sol.** p-Orbital is not present in H atom.

**Ex.41** A  $\sigma$  bond is formed in  $O_2$  by overlapping of :

- [1]  $2p_y - 2p_z$               [2]  $2p_y - 2s$               [3]  $2p_z - 2s$               [4]  $2p_z - 2p_z$               **Ans. [4]**

**Sol.** Extent of  $p_y - p_z$  and  $p_y - s$  overlapping is zero.

**Ex.42** Which of the following orbitals will form a weak bond by the overlapping ?

- [1]  $sp^2 - sp^2$               [2]  $sp^2 - s$               [3]  $s - s$                       [4] p - p (coaxial)              **Ans. [3]**

**Sol.** Due to non directional character of s orbital, bond formed by s-s orbitals will be weak.

**Ex.43** Which of the following overlapping will form a  $\pi$  bond ?

- [1] sp-p                      [2]  $sp^2 - s$                       [3]  $sp^3 - sp^3$                       [4] None of these              **Ans. [4]**

**Sol.** Hybrid orbitals always form a  $\sigma$  bond.

### 13. VALENCE BOND THEORY

This theory was first put forward by **Heitler and London** in 1927.

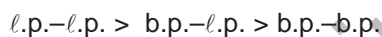
(i) Covalent bond is formed between atoms by sharing of unpaired electrons of the outermost shell in order to attain greater stability.

(ii) The valency of an element depends on the number of unpaired electrons in its outermost orbit.

In order to explain bond angle and geometry of molecules, valence shell electron pair repulsion theory was forward by Gillespie and Nyholm.

- (iii) The valency of an element depends on the number of unpaired electrons in its outermost orbit and the same number of bonds will be formed by overlapping of orbitals, e.g. 1 for F, 1 for H, etc.
- (iv) The elements, which have empty orbitals, can increase their covalency by excitation of electrons.
- (v) Orbitals of unpaired electrons come closer in such a direction that maximum overlapping can occur and stronger bond is formed.
- (vi) The electron cloud formed by overlapping is localized in between the two atoms.
- (vii) If unpaired electrons are present in different orbitals, the orbitals make hybrid orbitals by hybridization before bond formation and these hybrid orbitals form stronger  $\sigma$  bond by overlapping.
  - (i) Geometry of the molecule depends on the numbers of lone pairs and bond pairs on the central atom.
- (1) ***l.p.-l.p. Repulsion*** – When there are two *l.p.* on the central atom, the bond angle decreases due to *l.p.-l.p.* repulsion.
- (2) ***b.p.-l.p. Repulsion*** – When a *l.p.* is present on the central atom, this will repel *b.p.* so bond angle will decrease.

The decreasing order of repulsions is as follows



#### 14. HYBRIDIZATION

- (1) Hybridization occurs in the central atom of a compound, e.g. in  $\text{CH}_4$ ,  $\text{H}_2\text{O}$ .
- (2) Generally, the orbitals of the outermost shell of the central atom participate in hybridization.
- (3) In hybridization, all types of orbitals (empty and half-filled and fully-filled) can participate.
- (4) If the orbitals participating in hybridization have paired electrons, the new orbitals formed will also have paired electrons.
- (5) The  $\sigma$  bonds formed by hybrid orbitals are strong and their orientation is different in space.
- (6) All hybrid orbitals are generally identical having one larger lobe and one smaller lobe.
 

Total no. of hybrid orbitals = No. of  $\sigma$  bonds + No. of lone pairs
- (7) In hybridization, the orbitals of the outermost shell of central atom having almost equal energy, combine and form new hybrid orbitals of identical energy.
- (8) The number of hybrid orbitals formed will be equal to the number of orbitals participating in hybridization e.g. 2, 3 and 4 hybrid orbitals are formed in  $sp$ ,  $sp^2$  and  $sp^3$  hybridization, respectively.
- (9) Orbitals having unpaired electrons overlap for pairing and overlapping occurs in the orbitals having paired electrons.
- (10) Bond pair is formed by overlapping of hybrid orbitals. So lone pair or bond pair is present in a hybrid orbital.
- (11) The hybridization of central atom of a molecule can be determined by the following formula.

$$\text{Total no. of hybrid orbitals} = \text{No. of } \sigma \text{ bonds} + \text{No. of lone pairs}$$

- (12) Hybrid orbitals have directional property, so more the directional property of hybrid orbital, stronger will be the bond formed :  $sp < sp^2 < sp^3 < sp^3d < sp^3d^2 < sp^3d^3$

## 14.1 Types of Hybridisation

### $sp^3$ Hybridisation :

- (i) In this hybridisation, one s orbital and three p orbitals join up and form four  $sp^3$  hybrid orbitals of same energy.
- (ii) The geometry of the compound will be tetrahedral and bond angle will be about  $109^\circ 28'$ . e.g.  $CH_4$ ,  $CCl_4$  & Diamond

### $sp^2$ Hybridisation :

- (i) One s and two p orbitals join up and form three new  $sp^2$  hybrid orbitals.
- (ii) The geometry of the molecule will be trigonal and bond angle will be  $120^\circ$ .

Examples –  $BF_3$ ,  $BCl_3$ ,  $BH_3$ ,  $C_2H_4$  and graphite.

### $sp$ Hybridisation :

- (i) In  $sp$  hybridisation, one s orbital and one p orbital join up and form two  $sp$  hybrid orbitals of equal energy.
- (ii) Geometry of along  $sp$  hybrid orbital will be linear and bond angle will be  $180^\circ$ .
- (iii) Two  $\sigma$  bonds will be formed by  $sp$  hybridised atom.
- (iv) The dipole moment will be zero.

Examples –  $BeF_2$ ,  $BeCl_2$ ,  $C_2H_2$ ,  $CO_2$  etc.

### $sp^3 d$ Hybridisation :

One s, three p and one d orbitals join up and form five  $sp^3 d$  hybrid orbitals of same energy.

Example –  $PCl_5$ ,  $ClF_3$ ,  $SF_4$ ,  $XeF_2$ ,  $TeCl_4$ ,  $ICl_2^+$  etc.

### $sp^3 d^2$ Hybridisation :

One s, three p and two d orbitals combine and form six  $sp^3 d^2$  hybrid orbitals of same energy.

Example –  $SF_6$ ,  $ClF_5$ ,  $XeF_4$ ,  $IF_4$ ,  $SiF_6^{2-}$ ,  $ICl_4^-$ .

### $sp^3 d^3$ Hybridisation :

One s, three p and three d orbitals join up and form seven new  $sp^3 d^3$  hybrid orbitals of same energy.

Example –  $IF_7$ ,  $SeF_6$ , etc.

**Ex.44** Which of the following molecules is bent ?

[1]  $CO_2$

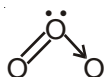
[2]  $O_3$

[3]  $N_2O$

[4] None of these

**Ans. [2]**

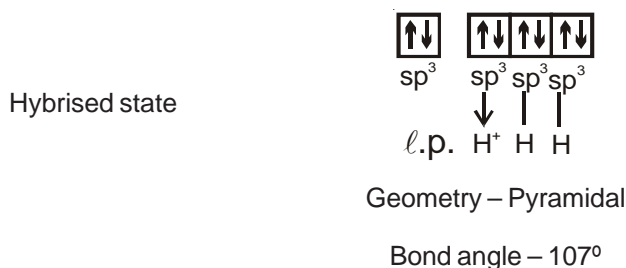
**Sol.**



**Ex.45** What is the type of hybridisation in  $H_3O^+$  ?

**Sol.** O atom is  $sp^3$  hybridised and has one lone pair. Its geometry is pyramidal.

Ground state  $O^0 = 1s^2, 2s^2 2p^4$



**Ex.46** Which of the following species is planar ?

- [1]  $\text{NH}_4^+$                       [2]  $\text{BF}_4^-$                       [3]  $\text{XeF}_4$                       [4]  $\text{SiCl}_4$                       **Ans. [3]**

**Sol.** Types of hybridisation are  $sp^3$  in  $\text{NH}_4^+$ ,  $\text{BF}_4^-$  and  $\text{SiCl}_4$  and  $sp^3d^2$  in  $\text{XeF}_4$ .

**Ex.47** Which of the following ions has tetrahedral geometry ?

- [1]  $\text{Na}^+$                       [2]  $\text{NH}_4^+$                       [3]  $\text{Mg}^{+2}$                       [4]  $\text{CO}_3^{-2}$                       **Ans. [2]**

**Sol.**  $\text{NH}_4^+$  is  $sp^3$  hybridisation so structure will be tetrahedral.

**Ex.48** What should be the geometry of the molecule when there are three bond pairs and one lone pair on the central atom ?

- [1] Tetrahedral                      [2] Pyramidal                      [3] Trigonal                      [4] Octahedral                      **Ans. [2]**

**Sol.** For example,  $\text{NH}_3$  has three N–H bond pair and one lone pair. Its geometry is trigonal pyramidal.

**Ex.49** Which of the following molecules has  $sp^2$  hybridisation on N atom ?

- [1]  $\text{NH}_3$                       [2]  $\text{NOCl}$                       [3]  $\text{N}_2\text{H}_4$                       [4] All of the above                      **Ans. [2]**

**Sol.** Nitrogen atom in  $\text{Cl}-\ddot{\text{N}}=\text{O}$  has one lone pair, two  $\sigma$  bond pairs and one  $\pi$  bond pair. So, N atom is in a state of  $sp^2$  hybridisation.

**Ex.50** If hybridisation on Co atom is  $sp^3d^2$ , the geometry of  $[\text{Co}(\text{NH}_3)_6]^{+3}$  will be similar to that of :

- [1]  $\text{SiF}_6^{-2}$                       [2]  $\text{SF}_6$                       [3] both 1 and 2                      [4] None of these                      **Ans. [3]**

**Sol.** S is in a state of  $sp^3d^2$  hybridisation in  $\text{SiF}_6^{-2}$  and  $\text{SF}_6$  and the geometry of  $sp^3d^2$  and  $d^2sp^3$  will be octahedral.

## 14.2 Hybridisation in Transition Metal Ions

In  $sp^3d$  hybridisation, d orbital of the outermost orbit participates. But in  $dsp^3$  hybridisation, the d orbital of inner orbit ( $n - 1$ ), which is vacant in transition elements, participates.

## 14.3 Hybridisation, Geometry of Some Molecules and Ions

S.No.	Molecule or Ion	Hybridisation	Geometry
1.	Diamond	$sp^3$	Tetrahedral
2.	$CH_4$	$sp^3$	Tetrahedral
3.	$H_2O$	$sp^3$	Angular
4.	$H_2Se$	$sp^3$	Angular
5.	$OF_2$	$sp^3$	Angular
6.	$Cl_2O$	$sp^3$	Angular
7.	$NH_3$	$sp^3$	Pyramidal
8.	$NF_3$	$sp^3$	Pyramidal
9.	$PH_3$	$sp^3$	Pyramidal
10.	$SO_4^{2-}$	$sp^3$	Tetrahedral
11.	$NH_4^+$	$sp^3$	Tetrahedral
12.	$H_3O^+$	$sp^3$	Pyramidal
13.	$BH_3$	$sp^2$	Trigonal planar
14.	$BCl_3$	$sp^2$	Trigonal planar
15.	$BF_3$	$sp^2$	Trigonal planar
16.	$CO_3^{2-}$	$sp^2$	Trigonal planar
17.	$NO_3^{-1}$	$sp^2$	Trigonal planar
18.	Graphite	$sp^2$	hexagonal layer structure
19.	$SO_3$	$sp^2$	Trigonal planar
20.	$SnX_2$	$sp^2$	Angular
21.	$BeCl_2$	$sp$	Linear
22.	$CO_2$	$sp$	Linear
23.	$ZnCl_2$	$sp$	Linear
24.	$HgCl_2$	$sp$	Linear
25.	$H-C \equiv N$	$sp$	Linear
26.	$N \equiv N \rightarrow O$	$sp$	Linear
27.	$PCl_5$	$sp^3d$	Trigonal bipyramid
28.	$SF_4$	$sp^3d$	Distorted trigonal Pyramidal
29.	$ClF_3$	$sp^3d$	T shaped
30.	$XeF_2$	$sp^3d$	Linear
31.	$ICl_2^{-1}$	$sp^3d$	Linear

## 15. MOLECULAR ORBITAL THEORY

- (a) There is another approach to chemical bonding known as molecular orbital theory (MOT) developed by Mulliken (1932) and Hund. Which explains the bonding characteristics in a better way.
- (b) The molecular orbital theory considers the entire molecule as a unit with all the electrons moving under the influence of all the nuclei present in the molecular.
- (c) This approach recognizes that each electron belongs to the molecule as a whole and may move within the entire molecule.

### 15.1 Important Features of M.O.T.

- (i) Like an A.O. (atomic orbital) which is around the nucleus of an atom there are M.O. (Molecular orbital) which are around the nuclei of a molecule.
- (ii) The molecular orbitals are entirely different from the atomic orbitals from which they are formed.
- (iii) The molecular orbitals possess different energy levels like atomic orbitals in an isolated atom.
- (iv) The shape of molecular orbitals are dependent upon the shapes of atomic orbitals from which they are formed.
- (v) Molecular orbitals are arranged in order of increasing energy just like atomic orbitals.
- (vi) The number of molecular orbitals formed is equal to the number of atomic orbitals combining in bond formation.
- (vii) Like atomic orbitals, the filling of electron in molecular orbitals is governed by the three principles such as Aufbau principle, Hund's rule and Pauli's exclusion principle.

### 15.2 Conditions for atomic orbitals to form M.O.

- (i) The combining A.O. should be a comparable energy
- (ii) The combining atomic orbitals must overlap to a large extent greater the overlap, stable is the molecule formed.

### 15.3 Different between A.O. and M.O.

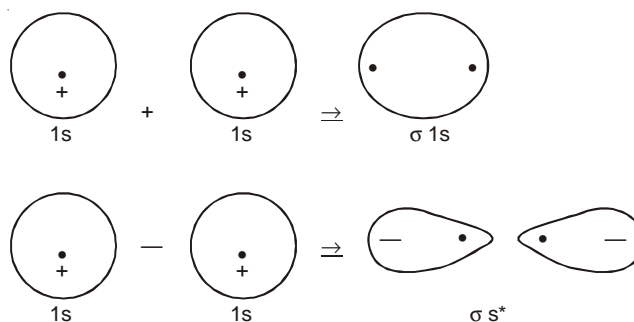
A.O. (Atomic orbital)	M.O. (Molecular Orbital)
1. An e <sup>-</sup> in an A.O. is under the influence of only one nucleus.	An e <sup>-</sup> in a M.O. is under the influence of nuclei of two or more atoms of a molecule.
2. Their existence is because of inherent property of the atoms	These are formed by the combination of atomic orbitals of comparable energies
3. They are less stable than bonding M.O. Which are more stable than antibonding M.O.	They are less or more stable than A.O.
4. They have simple shapes	They have complex shapes
5. They are represented by s, p, d, f	They are represented by $\sigma$ , $\sigma^*$ , $\pi$ , $\pi^*$ etc.

### 15.4 Formation of Bonding and Antibonding Molecular orbitals (LCAO method)

- (i) An electron in an atom is described by a wave function,  $\psi$  called an atomic orbitals. Similarly, the behavior of an electron in a molecule is described by a molecular wave function called molecular orbitals.
- (ii) Quantum mechanics shows that linear combination of two functions gives, not one but two combination and hence two molecule orbitals; a bonding orbital and an antibonding orbital.
- (iii) Such an orbital. Obviously cannot lead to the formation of a chemical bond and is therefore, termed as an antibonding M.O. combination of atomic orbitals-sigma ( $\sigma$ ) and Pi ( $\pi$ ) molecular orbitals.
- (iv) In the M.O. theory, orbitals are identified as  $\sigma$  or  $\pi$  depending upon the type of the symmetry of the molecular orbital.

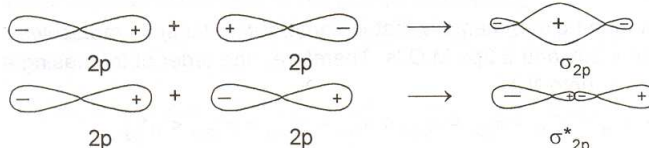


- (v) A sigma ( $\sigma$ ) M.O. is one that has cylindrical symmetry around the internuclear axis, i.e. it does not show any change of sign on rotation through  $180^\circ$  about the axis.
- (vi) It can be said that a sigma M.O. has no nodal plane (in which the electron density is zero) along the inter nuclear axis.

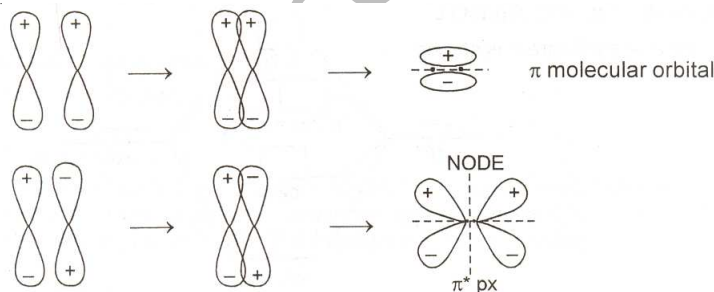


Formation of  $\sigma$  1s and  $\sigma^*$  is bonding anti bonding M.O.

- (vii) The bonding orbital is designated simply as  $\sigma$  orbital and antibonding as  $\sigma^*$ .
- (viii) Such a sigma ( $\sigma$ ) orbital is also formed when any two p-atom orbitals overlap in end-on (along their axes) position.



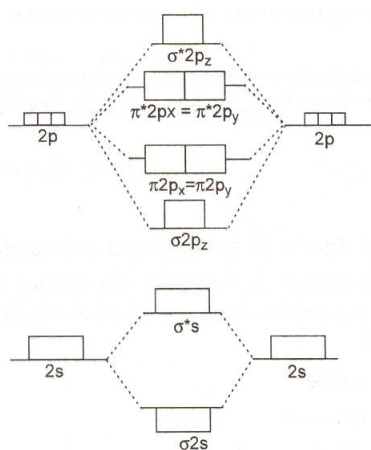
- (ix) Since the energy of a molecular orbital is directly related to the number of nodal planes, the  $\pi$ -orbital is more energetic than the  $\sigma$ -orbital. This explains why a  $\pi$ -bond is weaker than a  $\sigma$ -bond.



### 15.5 Relative energies of M.O. and filling of e<sup>-</sup>

- (i) Two general criteria, which determine the energy of the molecular orbitals are
- Initial energy of the atomic orbitals
  - The extent of the overlap of the atomic orbitals
- (ii) It is obvious that molecular orbitals formed from lower energy atomic orbitals have lower energy than the molecular orbitals formed from higher energy atomic orbitals.
- (iii) As the  $\sigma$  overlap is much more effective than  $\pi$ -overlap,  $\sigma$  p-molecular orbital is of lowest energy, even though originally all the three  $\pi$ -orbitals are of equal energy.
- (iv) The relative energies of the M.O. are obtained experimentally from spectroscopic data.
- (v) The sequence in the order of increasing energy is given below i.e., for more than  $N_2$ .

$$\sigma^{1s} < \sigma^{*1s} < \sigma^{2s} < \sigma^{*2s} < \sigma^{2p_z} < \pi^{2p_x} = \pi^{2p_y} < \pi^{*2p_x} = \pi^{*2p_y} < \sigma^{*2p_z}$$

M.O. Energy level diagram for  $O_2$ ,  $F_2$  and Ne.

- (vi) Using preceding figures for respective molecules as a guide, we can build up the electronic structure of simple diatomic molecules.
- (vii) The filling of electrons in various M.O. follows similar rules to those for filling A.O. similar M.O. belongs to entire molecule, the total number of electrons are taken into consideration and accommodated in molecular orbitals according to the following rules.
- Aufbau principle : The M.O. of lower energy is filled up first.
  - Pauli exclusion principles. Each M.O. can accommodate a maximum of two electrons having opposite spins.
  - Hund's rule. Whenever two equal energy M.O. are available electrons prefer to remain unpaired. This is particularly significant for  $\pi$ -orbitals because  $\pi$ -bonding and  $\pi$ -antibonding M.O. have equal energies.

### 15.6 Stability of Molecules

#### (A) Stability of molecules in terms of bonding and antibonding electrons :

- If  $N_b > N_a$ , the molecule is stable.
- If  $N_b < N_a$ , the molecule is unstable.
- Even if  $N_b = N_a$ , the molecule is unstable. This is due to the fact that antibonding effect is some what stronger than the bonding effect.

#### (B) Stability of molecules in terms of bond order :

- The relative stability of a molecule is further evaluated by a parameter known as bond order.
- It can be defined as number of covalent bonds formed in molecule.
- It is given by one half of the difference between the number of electrons in bonding orbitals and those in antibonding orbitals.

(d) Bond order =  $\frac{1}{2}$  [No. of electrons in bonding orbitals – No. of electrons in antibonding orbitals]

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

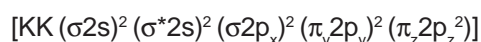
- The bond order of 1, 2 and 3 corresponds to single, double and triple bonds respectively. It may be mentioned that according to MO theory, even a fractional bond order is possible.
- Stability of molecule  $\propto$  bond order

- (g) Dissociation energy  $\propto$  bond order
- (h) bond length  $\propto \frac{1}{\text{bond order}}$
- (i) If all the electrons in a molecule are paired the substance is diamagnetic on the other hand if there are unpaired electron in the molecules, the substance is paramagnetic. More the number of unpaired electron in the molecule greater is the paramagnetism of the substance.

### 15.7 M.O. Configuration

(A) **Homonuclear diatomic species** : These types of ions have two identical atoms linked together of  $A_2$  type.

**$N_2$  :** (a) The electron configuration of N is  $1s^2, 2s^2, 2p^3$ . In  $N_2$  molecule, there are 14 electrons of which 4 are in K shell and are nonbonding. Each atom contributes four atomic orbitals and thus, the molecule consists of 8 M.O. Then ten electron are allotted to M.O. as follows



where KK denotes the closed K shell structure  $(\sigma 1s)^2(\sigma^* 1s)^2$

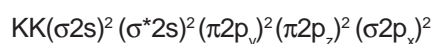
(b) Bond order  $\rightarrow \frac{1}{2}(8 - 2) = 3$

(c) Thus  $N_2$  molecule has three bonds, one sigma and two pi.

(B) **Heteronuclear diatomic molecules**

(a) **CO** : (a) We know that total number of valence electrons =  $8 + 6 = 14$

The distribution of electrons in various molecular orbitals of CO molecule is done in the following manner



(b) Bond order =  $\frac{1}{2}(8 - 2) = 3$

(c) It represents one sigma bond and two  $\pi$ -bonds (d) The molecule is stable and diamagnetic in nature.

## 16. HYDROGEN BOND

- (1) Hydrogen bond is formed in covalent compounds and not in ionic compounds.
- (2) H-bond is not formed in nonpolar covalent compounds.
- (3) H-bond is the attraction between H atom and strongly electronegative atom.

16.1 **Intermolecular Hydrogen Bond** : Bond between two nearest molecules.

(a) **Homointermolecular H-Bond** :

This type of H-bond is formed between same molecules. For example,  $H_2O$ , HF,  $NH_3$ , ROH,  $CH_3COOH$ , etc.

(b) **Heterointermolecular H-Bond** :

The type of H-bond is formed between molecules of different compounds.



16.2 **Intramolecular Hydrogen Bond** : Bond in a single molecule e.g. Nitrophenol

- (i) Due to higher electronegative in nature of O, electron density transfers from electron-rich  $O^{\delta-}$  to electron deficient  $H^{\delta+}$  bonded to the electronegative atom of the other molecule.
- (ii) H-bond is formed between two molecules, so this is called intermolecular H-bond.
- (iii) One  $H_2O$  molecule can form a maximum of four H-bonds.

## 17. SOME USEFUL FORMULAE

### Ionic character :

- (1)  $\propto$  Melting and boiling point    (2)  $\propto$  Solubility (Polar solvent)    (3)  $\propto$  Conductivity (Fused state)
- (4)  $\propto$  Size of cation    (5)  $\propto \frac{1}{\text{Size of anion}}$     (6)  $\propto \frac{1}{\text{Charge on cation \& anion}}$
- (7)  $\propto$  Inert configuration    (8)  $\propto \frac{1}{\text{Pseudo inert configuration}}$
- (9)  $\propto$  Difference in electronegativity of the covalently bonded atoms    (10)  $\propto$  Dipole moment

### Covalent character :

- (1)  $\propto \frac{1}{\text{Melting \& Boiling point}}$     (2)  $\propto \frac{1}{\text{Solubility}}$     (3)  $\propto \frac{1}{\text{Conductivity}}$
- (4)  $\propto \frac{1}{\text{Hardness}}$     (5)  $\propto \frac{1}{\text{Size of cation}}$     (6)  $\propto \text{Size of anion}$
- (7)  $\propto$  Charge an ions    (8)  $\propto \frac{1}{\text{Inert configuration}}$     (9)  $\propto$  Pseudo inert configuration
- (10)  $\propto \frac{1}{\text{Dipole moment}}$

### Bond length :

- (1)  $\propto$  Size of bonded atoms    (2)  $\propto \frac{1}{\text{Difference of electronegativity of bonded atoms}}$
- (3)  $\propto \frac{1}{\text{s Character in hybrid orbital}}$     (4)  $\propto$  p Character in hybrid orbital
- (5)  $\propto \frac{1}{\text{Resonance}}$

### Bond angle :

- (1)  $\propto \frac{1}{\text{Number of lone pair}}$     (2)  $\propto$  Electronegativity of central atom
- (3)  $\propto \frac{1}{\text{Electronegativity of terminal atom}}$     (4)  $\propto$  s character in hybrid orbitals

### Bond energy :

- (1)  $\propto \frac{1}{\text{Atomic size}}$     (2)  $\propto \frac{1}{\text{Bond length}}$     (3)  $\propto$  s character in hybrid orbitals
- (4)  $\propto$  difference of electronegativity values of bonded atoms    (5)  $\propto \frac{1}{\text{Lone pair present on bonded atom}}$