

# CHEMICAL BONDING

## INTRODUCTION

Atoms of different elements excepting noble gases do not have complete octet so they combine with other atoms to form chemical bond. The force which holds the atoms or ions together within the molecule is called a **chemical bond** and the process of their combination is called **Chemical Bonding**.

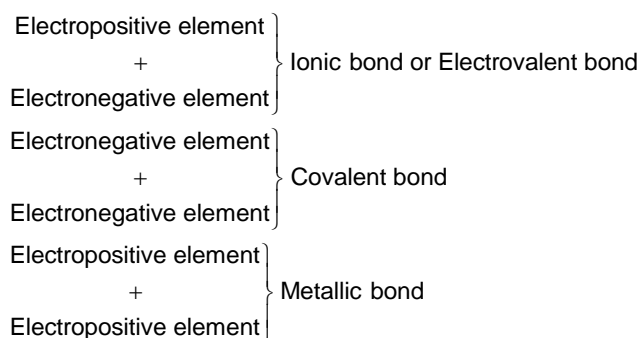
## CHEMICAL BOND

It is a type of very strong force of attraction that binds the two atoms (either similar or dissimilar) or ions together.

A molecule is formed if it is more stable and has lower energy than the individual atoms. Normally only electrons in the outermost shell of an atom are involved in bond formation and in this process each atom attains a stable electronic configuration of inert gas. Atoms may attain stable electronic configuration in three different ways by losing electrons, by gaining or by sharing electrons. The attractive forces which hold various constituents (atoms, ions etc) together in different chemical species are called chemical bond. Elements may be divided into three classes.

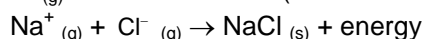
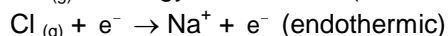
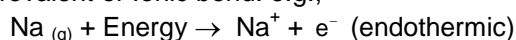
- Electropositive elements, whose atoms give up one or more electrons easily, they have low ionization potentials.
- Electronegative elements, which can gain electrons. They have higher value of electronegativity.
- Elements which have little tendency to lose or gain electrons.

Three different types of bond may be formed depending on electropositive or electronegative character of atoms involved.



## ELECTROVALENT OR IONIC BOND

The bond formed by the transfer of electron from electropositive element towards electronegative element is called electrovalent or ionic bond. e.g.,



## Factors favouring the formation of ionic Bond

- One of the atoms (the metal) must have a low ionization energy
- The other atom (non metal) must have high electron affinity.
- The electrostatic attraction between ions in the crystal i.e. lattice energy should be high.

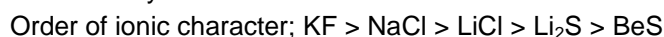
## Characteristics of Ionic Compounds

- |                                |                             |
|--------------------------------|-----------------------------|
| (i) Ionic crystalline geometry | (ii) Generally solid        |
| (iii) Soluble in polar solvent | (iv) Conductor in solution  |
| (v) High B.P and M.P.          | (vi) Non directional nature |

**Example 1.** The correct decreasing order of ionic character is:

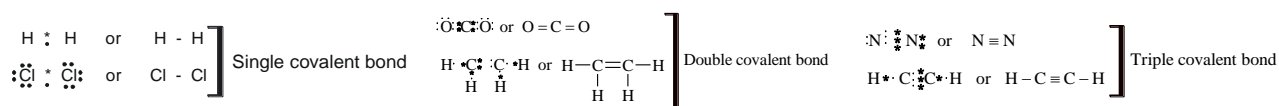
- |  |  |
|--|--|
| (a) $\text{BeS} > \text{Li}_2\text{S} > \text{LiCl} > \text{NaCl} > \text{KF}$ | (b) $\text{KF} > \text{NaCl} > \text{LiCl} > \text{Li}_2\text{S} > \text{BeS}$ |
| (c) $\text{NaCl} > \text{LiCl} > \text{KF} > \text{Li}_2\text{S} > \text{BeS}$ | (d) $\text{KF} > \text{LiCl} > \text{NaCl} > \text{BeS} > \text{Li}_2\text{S}$ |

**Solution.** (c)



## COVALENT BOND

Bond formed by the sharing of equal no. of electrons between the two concerned atoms is called covalent bond. It is represented as  $[\text{---}]$



Characteristics of covalent bond

- (i) Low M.P and B.P.
- (ii) Molecular geometry
- (iii) Bad conductor
- (iv) Soluble in non polar solvent
- (v) Directional nature

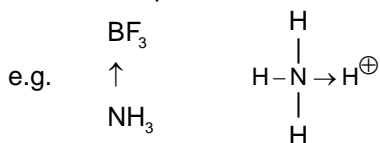
**The Lewis theory :** The tendency of atoms to achieve eight electrons in their outermost shell is known as lewis octet rule.

Lewis symbol for the representative elements are given in the following table,

Group	1	2	13	14	15	16	17
Group	IA	IIA	IIIA	IVA	VA	VIA	VIIA
Lewis symbol	X•	•X•	•X•	•X•	•X•	•X•	•X•

## CO-ORDINATE COVALENT, OR DATIVE BOND

The co-ordinate bond formation involves one sided sharing of a lone pair of electrons. The atom that donates the electron pair is known as donor and the atom which accepts the electron pair is called acceptor. e.g.



## ODD ELECTRON BOND

There are very small no. of stable compounds and ions which has unpaired oddelectron. e.g. NO, NO<sub>2</sub>, ClO<sub>2</sub>

## Comparison of ionic, covalent & coordinate compounds

Property	Ionic	Covalent	Coordinate
1. binding force	Between ions strong (coulombic)	Between molecules smaller (Vander Waal's)	in between
2. mp/bp	High	less than ionic	in between
3. condition	conductor of electricity in fused state & in aqueous solution	bad conductor	Greater than covalent
4. solubility in polar solvent (H <sub>2</sub> O)	High	Less	in between
5. Solubility in non polar solvent (ether)	Low	High	in between
6. Physical state	generally solid	liquid & gaseous	solid, liquid gas

**Example 2 :** Classify the following bonds as ionic, polar covalent or covalent and give your answer

- (a) Si Si bond in Cl<sub>3</sub> SiSiCl<sub>3</sub>
- (b) SiCl bond in Cl<sub>3</sub>SiSiCl<sub>3</sub>
- (c) CaF bond in CaF<sub>2</sub>
- (d) NH bond in NH<sub>3</sub>

**Solution:** (a) Covalent due to identical electronegativity

- (b) One electron pair is shared between Si & Cl and thus, covalent bond is expected but electron negativity of Cl is greater than that of Si & some polarity develops giving polar – covalent nature
- (c) Ionic since Ca completes its octet by transfer of two outershell electrons thus, completing their octets  
 $\text{Ca} [\text{Ar}]4s^2$ ,  $\text{F}[\text{He}]2s^22p^5$
- (d) Polar covalent, explanation as in (b)

## BOND PARAMETERS

- (A) Bond length:** It is the average distance between the centres of nuclei of the two bonded atoms
- The bond length increases with increasing in the size of the atoms. e.g. H–X bond length has the order  $\text{H} - \text{I} > \text{H} - \text{Br} > \text{H} - \text{Cl} > \text{H} - \text{F}$ .
  - A multiple bond (= or ) is always shorter than the corresponding single bond. ( $\text{C} = \text{C} < \text{C} - \text{C}$ )
  - Bond length decreases with the increase in s-character since an s-orbital is smaller than a p-orbital.
- (B) Bond Energy or Bond Strength**
- If bond is formed it involves release of certain amount of energy and an equivalent amount of energy is absorbed by breaking the bond.

## Remembering facts

- Most of the covalent bonds have energy between 50 to 100 K.cal mol<sup>-1</sup>.
- Bond energy increases from single to triple bond. i.e.,  $\text{C} - \text{C} < \text{C} = \text{C} < \text{C} \equiv \text{C}$
- The strength of bond is more than that of bond
- The bond energy decreases with the increase in no of lone pair in bonded atom. This is due to electrostatic repulsion between the lone pair of electrons on the two bonded atoms.

**Polarisation of Ionic Bond :** Cation pulls electron cloud slightly from anion and that's why its ionic character is decreased, i.e, the bond is polarised.

## FAJAN'S RULE

The magnitude of polarization or increased covalent character depends upon a number of factors. These factors are :

- Small size of cation :** Smaller size of cation greater is its polarizing power i.e. greater will be the covalent nature of the bond.
- Large size of anion :** Larger the size of anion greater is its polarizing power i.e. greater will be the covalent nature of the bond.
- Large charge on either of the two ions :** As the charge on the ion increases, the electrostatic attraction of the cation for the outer electrons of the anion also increases with the result its ability for forming the covalent bond increases.
- Electronic configuration of the cation :** For the two ions of the same size and charge, one with a pseudo noble gas configuration (i.e. 18 electrons in the outermost shell) will be more polarizing than a cation with noble gas configuration (i.e., 8 electron in outer most shell).

**Note :** Greater the polarisation of ionic bond. Lesser is its ionic character.

### Order of Polarisation :



**Polarisation of covalent bond :** Due to electronegativity difference between the bonded atoms shared electrons slightly shifts towards more electronegative atom, that's why bond become polarised.

**Note :** Greater the polarisation of covalent bond greater is its ionic character.

**Example 3 :** The decomposition temperature of  $\text{Li}_2\text{CO}_3$  is less than that of  $\text{Na}_2\text{CO}_3$ . Explain.

**Solution:** As  $\text{Li}^+$  ion is smaller than  $\text{Na}^+$  ion, thus small cation ( $\text{Li}^+$ ) will favour more covalent character in  $\text{Li}_2\text{CO}_3$  and hence it has lower decomposition temperature than that of  $\text{Na}_2\text{CO}_3$ .

### DIPOLE MOMENTS

A dipole consists of a positive and an equal negative charge separated by a distance within a molecule. The degree of polarity of a bond is given by the dipole moment ( $\mu$ ), which is the product of either charge ( $e$ ) and the distance ( $d$ ) between them.  $\mu = d \times e$ . 'e' is the electronic charge and  $d$  is the distance between the atomic centres.  $1 \text{ D} = 10^{-18} \text{ esu-cm} = 3.336 \times 10^{-30} \text{ C-m}$ .

### APPLICATIONS OF DIPOLE MOMENT MEASUREMENTS

- In determining the polarity of bonds:** As  $\mu = q \times d$ , obviously, greater is the magnitude of dipole moment, higher will be the polarity of the bond.
- In the calculation of percentage ionic character :** Taking the example of HCl, its dipole moment is 1.03 D. If HCl were 100% ionic, each end would carry charge equal to one unit viz  $4.8 \times 10^{-10} \text{ e.s.u.}$ . As bond length of HCl is  $1.275 \text{ \AA}$  its dipole moment for 100% ionic character would be

$$\begin{aligned}\mu_{\text{Ionic}} &= q \times d \\ &= 4.8 \times 10^{-10} \text{ e.s.u.} \times 1.275 \times 10^{-8} \text{ Cm} = 6.12 \text{ D} \\ \% \text{ ionic character} &= \frac{\mu_{\text{observed}}}{\mu_{\text{Ionic}}} = \frac{1.03}{6.12} \times 100 = 16.83\%\end{aligned}$$

**Example 4:** The resultant dipole moment of water is 1.85D ignoring the effects of lone pair. Calculate, the bond moment of each OH bond (given that bond angle in  $\text{H}_2\text{O} = 104^\circ$ ,  $\cos 104^\circ = -0.25$ )

**Solution:**

$$\begin{aligned}R^2 &= P^2 + Q^2 + 2PQ \cos \theta \\ (1.85)^2 &= x^2 + x^2 + 2x^2 \left( -\frac{1}{4} \right) \\ (1.85)^2 &= 2x^2 - \frac{x^2}{2} \Rightarrow \frac{3x^2}{2} \\ \therefore x &= 1.51 \text{ D}\end{aligned}$$

### FORMAL CHARGE ON AN ATOM IN A MOLECULE

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

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

### HYBRIDISATION

The phenomenon of mixing up of two or more atomic orbitals of nearly the same energies to form new type of orbitals is called hybridisation.

#### Rules of hybridization

- Only orbitals of nearly the same energies and belonging to the same atom or ion undergo hybridization.
- The no. of hybrid orbitals produced is equal to the number of atomic orbitals mixed during hybridization.
- Most of the hybrid orbitals are similar.
- The hybrid orbitals are distributed in space as far apart as possible.
- Hybrid orbital leads to the formation of sigma bonds only.

(vi) It is only a theoretical concept to explain the structure and shape of compounds.

**Table:** Geometry Shape of molecules/ion containing bond and lone pair

No. of b.p. of Electron	Hybridisation	Lone pair	Bond angle	expected geometry	Shape of compound	Example
2	sp	0	180°	Linear	Linear	BeF <sub>2</sub> , BeCl <sub>2</sub> , CO <sub>2</sub> , HgCl <sub>2</sub> , HCN, MgCl <sub>2</sub> , C <sub>2</sub> H <sub>2</sub> , [Ag(NH <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup>
3	sp <sup>2</sup>	0	120°	Trigonal planar	Trigonal planar	BF <sub>3</sub> , BCl <sub>3</sub> , BH <sub>3</sub> , AlCl <sub>3</sub> , SO <sub>3</sub> , C <sub>2</sub> H <sub>4</sub> , NO <sub>3</sub> <sup>-</sup> , CO <sub>3</sub> <sup>2-</sup> , C <sub>6</sub> H <sub>6</sub>
2	sp <sup>2</sup>	1	–	Trigonal Planar	V-shaped	SO <sub>2</sub> , SnCl <sub>2</sub> , NO <sub>2</sub> <sup>-</sup>
4	sp <sup>3</sup>	0	109°28'	Tetrahedral	Tetrahedral	SiCl <sub>4</sub> , SnCl <sub>4</sub> , CH <sub>4</sub> , SO <sub>4</sub> <sup>2-</sup> , ClO <sub>4</sub> <sup>-</sup> , PO <sub>4</sub> <sup>3-</sup>
3	sp <sup>3</sup>	1	≈107°	Tetrahedral	Pyramidal	NH <sub>3</sub> , NF <sub>3</sub> , PCl <sub>3</sub> , PH <sub>3</sub>
2	sp <sup>3</sup>	2	≈105°	Tetrahedral	V-shaped	H <sub>2</sub> O, H <sub>2</sub> S, PbCl <sub>2</sub> , OF <sub>2</sub>
4	dsp <sup>2</sup>	0	90°	Square planar	Square planar	[Ni(CN) <sub>4</sub> ] <sup>2-</sup> , [PtCl <sub>4</sub> ] <sup>2-</sup> , [Cu(NH <sub>3</sub> ) <sub>4</sub> ] <sup>++</sup>
5	sp <sup>3</sup> d	0	90°, 120°	TBP	TBP	PCl <sub>5</sub> , SbCl <sub>5</sub>
4	sp <sup>3</sup> d	1	109°28'	TBP	Triangular pyramidal	SF <sub>4</sub>
3	sp <sup>3</sup> d	2	90°	TBP	T-shape	ICl <sub>3</sub> , ClF <sub>3</sub>
2	sp <sup>3</sup> d	3	180°	TBP	Linear	XeF <sub>2</sub>
6	sp <sup>3</sup> d <sup>2</sup>	0	90°	Octahedral	Octahedral	SF <sub>6</sub> , SeF <sub>6</sub> , PF <sub>6</sub> <sup>-</sup> , SnCl <sub>6</sub> <sup>2-</sup>
5	sp <sup>3</sup> d <sup>2</sup>	1	90°	Octahedral	Square Pyramidal	ICl <sub>5</sub>
4	sp <sup>3</sup> d <sup>2</sup>	2	90°	Octahedral	Square planar	XeF <sub>4</sub> , ICl <sub>4</sub> <sup>-</sup>
7	sp <sup>3</sup> d <sup>3</sup>	0	72°, 90°	Pentagonal bipyramidal	PBP	IF <sub>7</sub>

**TBP = Trigonal Bypyramidal**

**PBP = Pentagonal bipyramidal**

**Example 5.** Predict the hybridization for the central atom in POCl<sub>3</sub>, OSF<sub>4</sub>, OIF<sub>5</sub>

**Solution:** POCl<sub>3</sub> Total No. of V.E. =  $\frac{5 + 6 + 21}{8} = \frac{32}{8} = 4$

So, hybridization = sp<sup>3</sup>

OSF<sub>4</sub> =  $\frac{6 + 6 + 28}{8} = \frac{40}{8} = 5$

So, hybridization of s = dsp<sup>3</sup>

OIF<sub>5</sub> =  $\frac{6 + 7 + 35}{8} = \frac{48}{8} = 6$

So, hybridization of I = d<sup>2</sup>sp<sup>3</sup>

### VALENCE BOND THEORY (VBT)

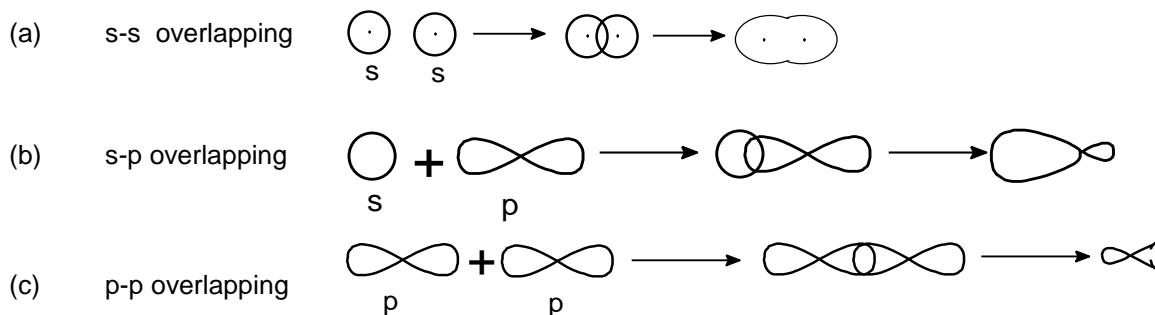
It was developed by Heitler and London in 1927 and modified by Pauling and Slater in 1931.

- (1) To form a covalent bond, two atoms must come close to each other so that orbitals of one overlaps with the other.
- (2) Orbitals having unpaired electrons of anti spin overlaps with each other.
- (3) After overlapping a new localized bond orbital is formed which has maximum probability of finding electrons.
- (4) Covalent bond is formed due to electrostatic attraction between radii and the accumulated electrons cloud and by attraction between spins of anti spin electrons.
- (5) Greater is the overlapping, lesser will be the bond length, more will be attraction and more will be bond energy and the stability of bond will also be high.
- (6) The extent of overlapping depends upon: Nature of orbitals involved in overlapping, and nature of overlapping.
- (7) More closer the valence shells are to the nucleus, more will be the overlapping and the bond energy will also be high.

- (8) Between two sub shells of same energy level, the sub shell more directionally concentrated shows more overlapping. Bond energy :  $2s-2s < 2s-2p < 2p-2p$
- (9) s-orbitals are spherically symmetrical and thus show only head on overlapping. On the other hand, p-orbitals are directionally concentrated and thus show either head on overlapping or lateral overlapping. Overlapping of different type gives sigma ( $\sigma$ ) and pi ( $\pi$ ) bond.

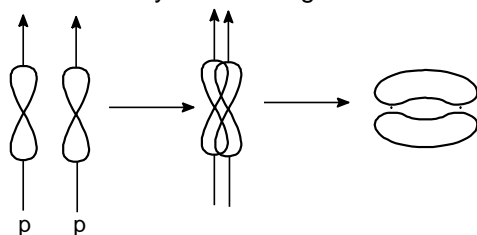
### $\sigma$ BOND

- It results from the head on overlapping of orbital
- The bond orbital consists of a single electron cloud symmetrically about internuclear axes.
- Provided the groups or atoms are smaller in size, they can undergo torsional rotation about single bonds.
- The shape of molecule is determined by the total no. of  $\sigma$ -bonds present in the molecule.
- $\sigma$ -bond can have independent existence



### $\pi$ BOND

- Its results from the side ways overlapping of two p-orbitals.
- Its bond orbital consists of two electron clouds one above and other below the plane of participating atoms.
- In  $\pi$ -bond the electron are held less firmly and can be more easily dissociated or polarized.
- Due to resistance to rotation around the bond, the group attached to it are not free to rotate.
- $\pi$ -bonding does not affect the shape of the molecule in which it occurs.
- $\pi$ -bond always exist along with  $\sigma$ -bond.

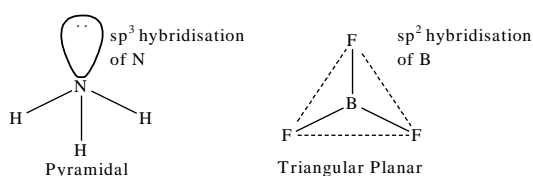


- Example 6.**  $\text{NF}_3$  is pyramidal while  $\text{BF}_3$  is triangular planar due to
- N is  $sp^2$  hybridised while B is  $sp^3$  hybridised
  - N is  $sp^3$  hybridised while B is  $sp^2$  hybridised
  - N has 4 electron pair while B has 3 electron pair
  - Both (b) and (c) are correct

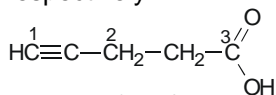
**Solution.**

(b) In  $\text{NF}_3$  nitrogen involves  $sp^3$  hybridisation and one position is occupied by a lone pair.

Therefore, the molecule is pyramidal. But in  $\text{BF}_3$ , B involves  $sp^2$  hybridisation having triangular planar geometry.



**Example 7.** State the hybridization of carbon atoms numbered 1, 2 and 3. Due to electronegativity difference respectively



(a)  $sp, sp^3, sp^2$   
 (c)  $sp^3, sp^2, sp$

(b)  $sp, sp^2, sp^3$   
 (d)  $sp^2 > sp^3 > sp$

**Solution:**

(a)  
 $C^1 = sp$   
 $C^2 = sp^3$   
 $C^3 = sp^2$

## VALENCE SHELL ELECTRON PAIR REPULSION (VSEPR) THEORY (SHAPES AND GEOMETRY OF MOLECULES)

Molecules exist in a variety of shapes. A number of physical and chemical properties of molecules arise from and are affected by their shapes. For example, the angular shape of the water molecules explains its many characteristic properties while a linear shape does not.

The determination of the molecular geometry and the development of theories for explaining the preferred geometrical shapes of molecules is an integral part of chemical bonding. The **VSEPR** theory (model) is a simple treatment for understanding the shapes of molecules.

Strictly speaking VSEPR theory is not a model of chemical bonding. It provides a simple recipe for predicting the shapes of molecules. It, in fact, is an extension of the Lewis interpretation of bonding and is quite successful in predicting the shapes of simple polyatomic molecules.

### The basic assumptions of the VSEPR theory are that:

Pairs of electron in the valence shell of a central atom repel each other

1. These pairs of electrons tend to occupy position in space that minimize repulsions and thus maximize distance between them.
2. The valence shell is taken as a sphere with the electron pairs localizing on the spherical surface at maximum distance from one another.
3. A multiple bonds are treated as a single super pair.
4. Where two or more resonance structures can depict a molecule, the VSEPR model is applicable to any such structures

For the prediction of geometrical shapes of molecules with the help of VSEPR model, it is convenient to divide molecules into two categories

### Regular Geometry

Molecules in which the central atom has no lone pairs

### Irregular Geometry

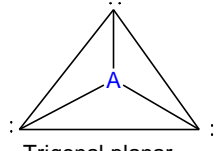
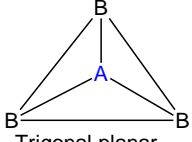
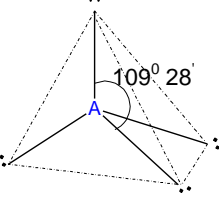
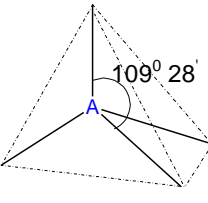
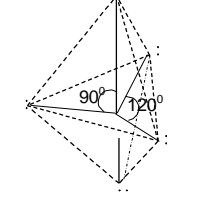
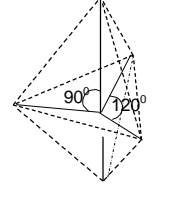
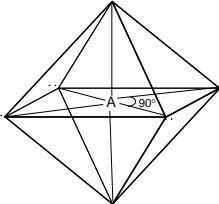
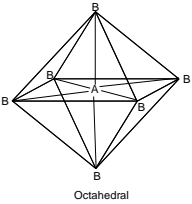
Molecules in which the central atom has one or more lone pairs, the lone pair electron in molecules occupy more space as compared to the bonding pair electrons. This causes greater repulsion between lone pairs of electrons as compared to the bond pairs repulsions. The descending order of repulsion

$(lp - lp) > (lp - bp) > (bp - bp)$

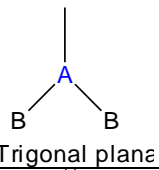
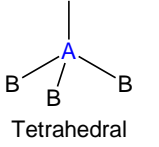
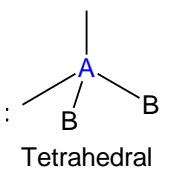
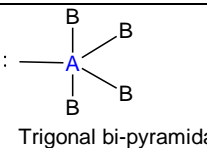
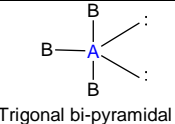
where lp-Lone pair; bp-bond pair

### Regular Geometry

Number of electron pairs	Arrangement of electrons	Molecular geometry	Examples
2		<b>B - A - B</b> <b>Linear</b>	BeCl <sub>2</sub> , HgCl <sub>2</sub>

3	 <p>Trigonal planar</p>	 <p>Trigonal planar</p>	$\text{BF}_3, \text{AlCl}_3$
4	 <p><math>109^\circ 28'</math></p>	 <p><math>109^\circ 28'</math></p>	$\text{CH}_4, \text{NH}_4^+, \text{SiF}_4$
5	 <p><math>90^\circ</math> <math>120^\circ</math></p> <p>trigonal bipyramid</p>	 <p><math>90^\circ</math> <math>120^\circ</math></p> <p>trigonal bipyramid</p>	$\text{PCl}_5, \text{PF}_5$
6	 <p><math>90^\circ</math></p>	 <p>Octahedral</p>	$\text{TeF}_6$

### Irregular Geometry

Molecule Type	No. of Bonding pairs	No. of lone pair	Arrangement of electrons pairs	Shape (Geometry)	Examples
$\text{AB}_2\text{E}$	2	1	 <p>Trigonal plane</p>	Bent	$\text{SO}_2, \text{O}_3$
$\text{AB}_2\text{E}$	3	1	 <p>Tetrahedral</p>	Trigonal pyramidal	$\text{NH}_3$
$\text{AB}_2\text{E}_2$	2	2	 <p>Tetrahedral</p>	Bent	$\text{H}_2\text{O}$
$\text{AB}_4\text{E}$	4	1	 <p>Trigonal bi-pyramidal</p>	See saw	$\text{SF}_4$
$\text{AB}_3\text{E}_2$	3	2	 <p>Trigonal bi-pyramidal</p>	T-shaped	$\text{ClF}_3$



$AB_5E$	5	1	<p>Octahedral</p>	Square pyramidal	$BrF_5$
$AB_4E_2$	4	2	<p>Octahedral</p>	Square planar	$XeF_4$

**Example 8.** Why the bond angle of H – C – H in methane ( $CH_4$ ) is  $109^\circ 28'$  while H – N – H bond angle in  $NH_3$  is  $107^\circ$  though both carbon and nitrogen are  $sp^3$  hybridized

**Solution:** In  $CH_4$  there are 4 bond pair of electrons while in  $NH_3$  are 3 bond pair of electrons and 1 lone pair of electrons. Since bond pair bond pair repulsion is less than lone pair bond pair repulsion, in  $NH_3$  bond angle is reduced from  $109^\circ 28'$  to  $107^\circ$ .

### PERCENTAGE OF IONIC CHARACTER

Every ionic compound having some percentage of covalent character according to Fajan's rule. The percentage of ionic character in a compound having some covalent character can be calculated by the following equation.

$$\text{The percent ionic character} = \frac{\text{Observed dipole moment}}{\text{Calculated dipole moment assuming 100\% ionic bond}} \times 100$$

**Example 9.** Calculate the % of ionic character of a bond having length =  $0.92 \text{ \AA}$  and  $1.91 \text{ D}$  as it's observed dipole moment.

**Solution:** To calculate  $\mu$  considering 100% ionic bond

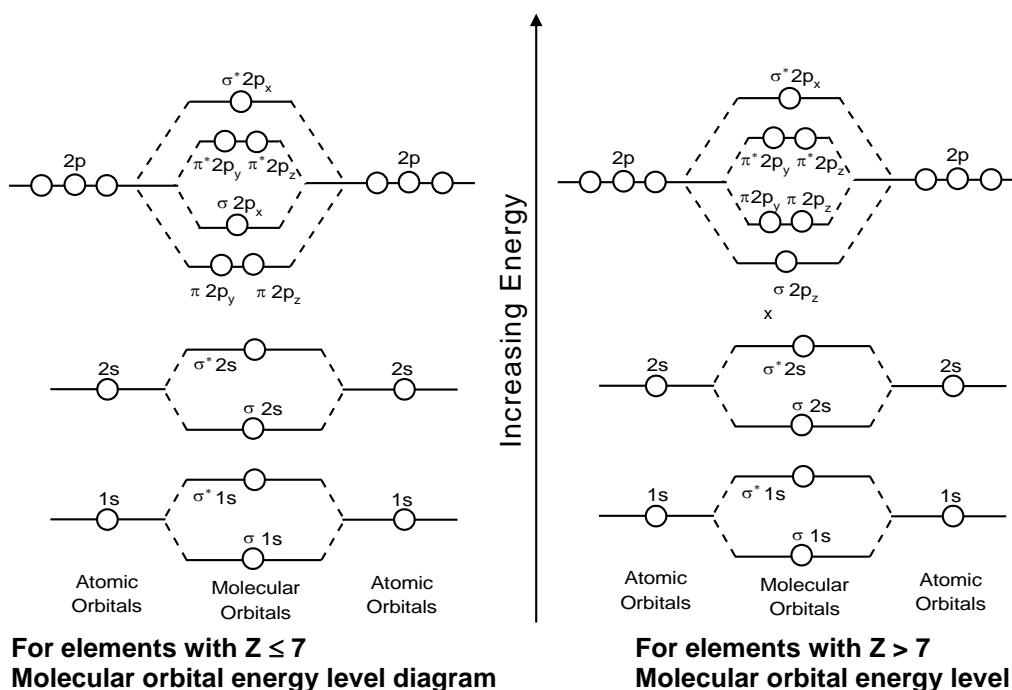
$$= 4.8 \times 10^{-10} \times 0.92 \times 10^{-8} \text{ esu cm}$$

$$= 4.8 \times 0.92 \times 10^{-18} \text{ esu cm} = 4.416 \text{ D}$$

$$\therefore \% \text{ ionic character} = \frac{1.91}{4.416} \times 100 = 43.25$$

### MOLECULAR ORBITAL THEORY

- There is another approach to chemical bonding known as molecular orbital theory (MOT) developed by Mulliken (1932) and Hund. Which explains the bonding characteristic in a better way.
- 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 molecule.
- This approach recognizes that each electron belongs to the molecule as a whole and may move within the entire molecule.



## IMPORTANT FEATURES OF M.O.T

1. 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.
2. The molecular orbitals possess different energy levels like atomic orbitals from which they are formed.
3. The molecular orbitals possess different energy levels like atomic orbitals in an isolated atom.
4. The shape of molecular orbitals are dependent upon the shapes of atomic orbitals from which they are formed.
5. Molecular orbitals are arranged in order of increasing energy just like atomic orbitals.
6. The number of molecular orbitals formed is equal to the number of atomic orbitals combining in bond formation.
7. 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.

## Conditions for Atomic Orbitals to Form M.O.

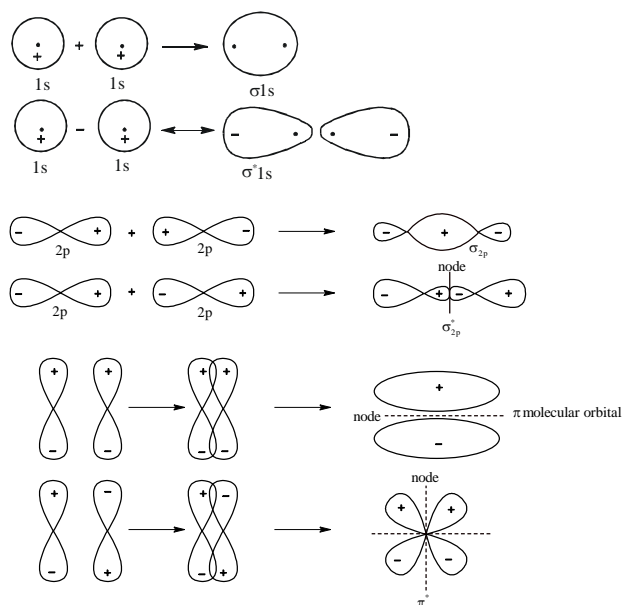
1. The combining A.O. should have comparable energy
2. The combining atomic orbitals must overlap to a large extent. Greater the overlap, stable is the molecule formed.

## Formation of Bonding and Antibonding Molecular Orbitals (LCAO method)

(a) An electron in an atom is described by a wave function, called an atomic orbitals. Similarly, the behavior of an electron in a molecule is described by a molecular wave function called molecular orbitals.

(b) Quantum mechanics shows that linear combination of two functions gives, not one but two combination and hence two molecular orbitals are formed a bonding orbital and another an anti-bonding orbital.

(c) A sigma ( $\sigma$ ) M.O. is one that has cylindrical symmetry around the inter nuclear axis.



(A) **Aufbau's order of increasing energy for**  
 $H_2, He_2, Li_2, Be_2, B_2, C_2, N_2$  etc.

$$\sigma(1s) < \sigma^*(1s) < \sigma(2s) < \sigma^*(2s) < \pi(2p_x) = \pi(2p_y) < \sigma(2p_z) < \pi^*(2p_x) = \pi^*(2p_y) < \sigma^*(2p_z)$$

(B) **Aufbau's order of increasing energy for**  
 $O_2, F_2, Ne_2, NO$  etc.

$$\sigma(1s) < \sigma^*(1s) < \sigma(2s) < \sigma^*(2s) < \sigma(2p_z) < \pi(2p_x) = \pi(2p_y) < \pi^*(2p_x) = \pi^*(2p_y) < \sigma^*(2p_z)$$

## Stability of Molecules

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

- (i) If  $N_b > N_a$ , the molecule is stable
- (ii) If  $N_b < N_a$ , the molecule is unstable.

$$\text{Bond order} = \frac{N_b - N_a}{2}$$

- (a) Larger the bond order, smaller is the bond length and larger is the bond strength
- (b) Molecule having negative or zero bond order does not exist.

**Example 10.** Correct order of bond energy is:

- (A)  $N_2 > N_2^+ > N_2^- > N_2^{2-}$
- (B)  $N_2^+ > N_2^- > N_2^{2-} > N_2$
- (C)  $N_2 > N_2^- = N_2^+ > N_2^{2-}$
- (D)  $N_2^- > N_2 = N_2^+ > N_2^{2-}$

**Solution:**

Bond order of  $N_2 = 3$ ,  $N_2^+ = 2.5$ ,  $N_2^- = 2.5$ ,  $N_2^{2-} = 2$

But  $N_2^-$  has more electrons in ABMO than  $N_2^+$  so correct order of bond energy will be  $N_2 > N_2^+ > N_2^- > N_2^{2-}$

## HYDROGEN BOND

A hydrogen atom normally forms a single bond. In some compounds, however, the hydrogen atom may be located between two atoms acting as a bridge between them. Hydrogen atom is now involved in two bonds, one a normal covalent bond, the other a hydrogen bond. A hydrogen bond is always formed between two small, strongly electronegative atoms such as fluorine, oxygen and nitrogen.

### Conditions For Hydrogen Bonding

- (i) The molecule must contain a highly electronegative atom linked to hydrogen atom.
- (ii) The size of electronegative atom should be small. These conditions are met only by F, O and N atoms.

Although Cl has the same electronegativity as nitrogen, it does not form effective hydrogen bond. This is because of its larger size than that of N with the result that its electrostatic attractions are weak.

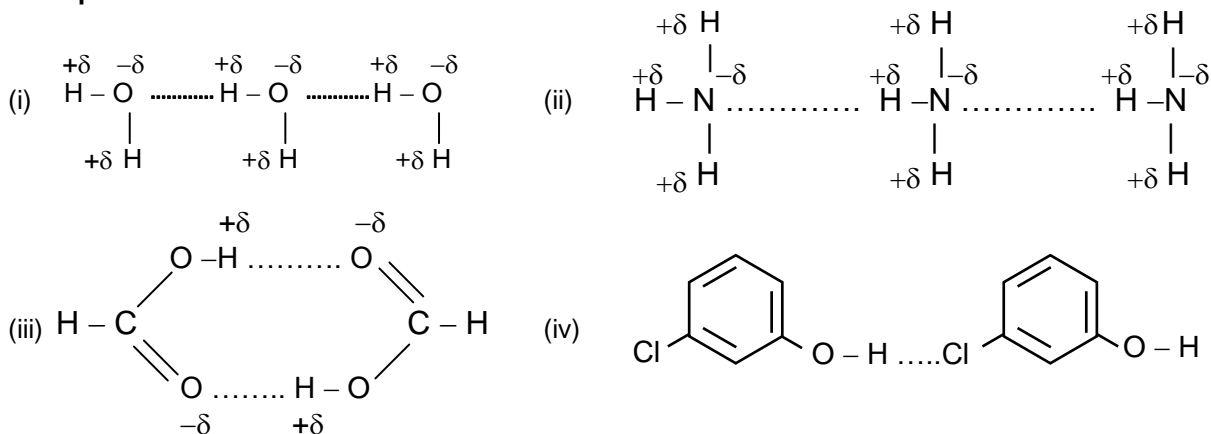
### Types of Hydrogen Bonding

Generally the hydrogen bonds are classified into two types.

### Intermolecular Hydrogen Bonding

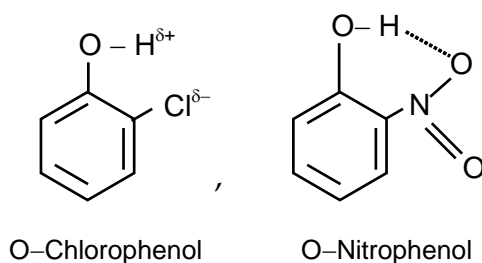
In such types of hydrogen bonding the two or more than two molecules of same or different compounds combine together to give a polymeric aggregate.

**For example.**



### Intramolecular Hydrogen Bonding

In this type, hydrogen bonding occurs within two atoms of the same molecule. This type of hydrogen bonding is commonly known as chelation and frequently occurs in organic compounds.



**Example 11.**  $\text{H}_2\text{O}$  is a liquid at ordinary temperature while  $\text{H}_2\text{S}$  is a gas although both O and S belong to the same group of the periodic table.

**Solution:**  $\text{H}_2\text{O}$  is capable of forming intermolecular hydrogen bonds. This is possible due to high electronegativity and small size of oxygen. Due to intermolecular H-bonding, molecular association takes place. As a result the effective molecular weight increases and hence the boiling point increases. So  $\text{H}_2\text{O}$  is a liquid. But in  $\text{H}_2\text{S}$  no hydrogen bonding is possible due to large size and less electronegativity of S. So its boiling point is equal to that of an isolated  $\text{H}_2\text{S}$  molecule and therefore it is a gas.

### INERT PAIR EFFECT

Heavier p-block and d-block elements show two oxidation states. One is equal to group number and second is group number minus two. For example  $\text{Pb}(5s^2 5p^2)$  shows two OS, +II and +IV. Here +II is more stable than +IV which arises after loss of all four valence electrons. Reason given for more stability of +II O.S. that  $5s^2$  electrons are reluctant to participate in chemical bonding because bond energy released after the bond formation is less than that required to unpair these electrons (lead forms a weak covalent bond because of greater bond length).

**Example 12.** Why does  $\text{PbI}_4$  not exist?

**Solution:**  $\text{Pb}(+IV)$  is less stable than  $\text{Pb}(+II)$  due to inert pair effect and therefore  $\text{Pb}(+IV)$  is reduced to  $\text{Pb}(+II)$  by  $\text{I}^-$  which changes to  $\text{I}_2$  ( $\text{I}^-$  is a good reducing agent)