

# Chemical Bonding and Molecular Structure

## Topic 1

1. The attractive force which holds various constituents (atoms, ions, etc.) together in different chemical species is called a chemical bond. The formation of chemical compounds takes place as a result of combination of atoms in different ways. The atoms interact with each other on account of following reasons :

(i) **Lowering of energy of combining atoms** : The process of bonding between the atoms decreases the energy of the combining atoms and gives rise to the formation of a system which has lower energy and hence has greater stability.

(ii) **Lewis octet rule** : Octet theory of valency or electronic theory of valency states that in the formation of a chemical bond, atoms interact with each other by losing, gaining or sharing of electrons so as to acquire a stable outer shell of eight electrons. The tendency of atoms to achieve eight electrons in their outermost shell is known as Lewis octet rule.

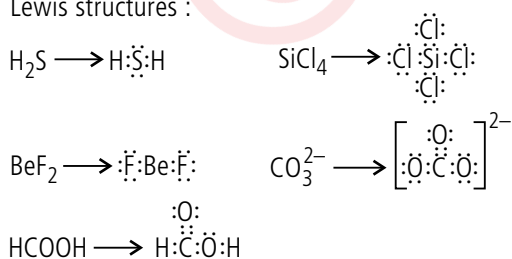
2. Lewis dot symbols :

- (i)  $\text{Mg} \longrightarrow \cdot\text{Mg}\cdot$                       (ii)  $\text{Na} \longrightarrow \text{Na}\cdot$   
 (iii)  $\text{B} \longrightarrow \cdot\text{B}\cdot$                               (iv)  $\text{O} \longrightarrow \cdot\ddot{\text{O}}\cdot$   
 (v)  $\text{N} \longrightarrow \cdot\ddot{\text{N}}\cdot$                               (vi)  $\text{Br} \longrightarrow \cdot\ddot{\text{Br}}\cdot$

3. Lewis symbols :

- (i)  $\text{S} \longrightarrow \cdot\ddot{\text{S}}\cdot$  ;  $\text{S}^{2-} \longrightarrow [\cdot\ddot{\text{S}}\cdot]^{2-}$   
 (ii)  $\text{Al} \longrightarrow \cdot\ddot{\text{Al}}\cdot$  ;  $\text{Al}^{3+} \longrightarrow [\text{Al}]^{3+}$   
 (iii)  $\text{H} \longrightarrow \dot{\text{H}}$  ;  $\text{H}^- \longrightarrow \ddot{\text{H}}^-$

4. Lewis structures :



5. **Octet rule** : The tendency of atoms in molecules to have eight electrons in their valence shells (two for hydrogen atom) is known as the octet rule.

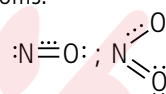
**Significance** :

- (i) It explains the formation of most of the compounds.  
 (ii) It is quite useful for understanding the structures of most of the organic compounds.

**Limitations** :

(i) In some compounds, the number of electrons surrounding the central atom is less than eight *e.g.*,  $\text{LiCl}$ ,  $\text{BeH}_2$  and  $\text{BCl}_3$ .

(ii) In molecules with an odd number of electron like nitric oxide ( $\text{NO}$ ) and nitrogen dioxide ( $\text{NO}_2$ ), the octet rule is not satisfied for all the atoms.



(iii) In a number of compounds there are more than eight valence electrons around the central atom. This is termed as the expanded octet. Some of the examples of such compounds are  $\text{PF}_5$ ,  $\text{SF}_6$ ,  $\text{H}_2\text{SO}_4$  and a number of coordination compounds.

6. The following factors facilitate the formation of an ionic bond between a metal and a non-metal :

(i) **Ionisation energy** : Lesser the ionisation energy, greater is the ease of formation of a cation.

(ii) **Electron affinity** : High electron affinity favours formation of an anion.

(iii) **Lattice energy** : The higher the magnitude of the lattice energy, the greater is the tendency for the formation of an ionic bond.

7. Greater the bond order, shorter is the bond length and so, higher is the bond strength.

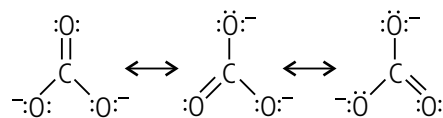
8. The equilibrium distance between the centres of the nuclei of two atoms bonded together is termed as bond length or bond distance.

Bond length in ionic compounds =  $r_c^+ + r_a^-$

Bond length in covalent compounds ( $AB$ ) =  $r_A + r_B$

9. Whenever a single Lewis structure cannot describe a molecule accurately, a number of structures with similar energy, positions of nuclei, bonding and non-bonding pairs of electrons, known as the canonical forms of the hybrid are taken, which describe the molecule accurately. This phenomenon is known as resonance.

Resonance hybrid structures of carbonate ion are shown as follows :



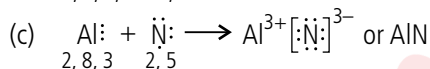
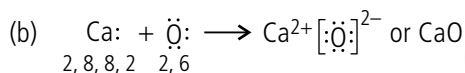
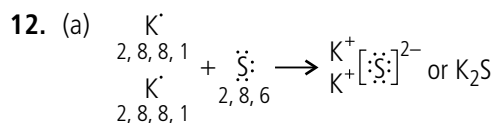
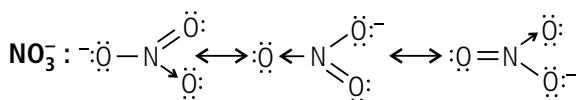
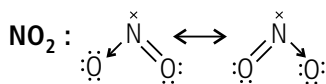
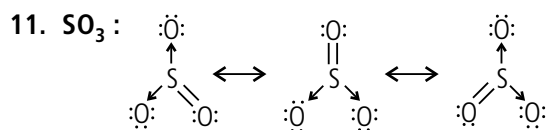
(i) The relative position of all the atoms in each of the canonical form is same.

(ii) The number of unpaired and paired electrons in each of the canonical form is same.

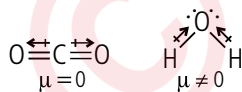
(iii) Negative charge is residing on more electronegative atom.

(iv) As a result of resonance, bond length and bond order is same.

10. These two cannot be called as canonical forms as relative position of hydrogen is changed. In resonance, canonical forms should differ only in the position of electrons and not in the position of atoms.



13. Even though both  $\text{CO}_2$  and  $\text{H}_2\text{O}$  are triatomic, but  $\text{CO}_2$  has zero dipole moment. It implies that  $\text{CO}_2$  has a symmetrical structure which is possible only when it is linear. However,  $\text{H}_2\text{O}$  has a net dipole moment suggesting that the molecule is non-linear.



14. Applications of dipole moment are :

(i) **To decide polarity of the molecule** : Molecules having zero dipole moment are said to be non-polar molecules and those having  $\mu_R \neq 0$ , are polar in nature.

(ii) **To determine percentage of ionic character** :

Percentage of ionic character

$$= \frac{\text{Experimental value of dipole moment}}{\text{Theoretical value of dipole moment}} \times 100$$

(iii) **To determine geometry of molecules** : The values of dipole moments provide valuable information about the structures of molecules.

(a)  $\text{CO}_2$ ,  $\text{CS}_2$  are linear as values of their dipole moments are zero.

(b)  $\text{H}_2\text{O}$  is non-linear as it has a net dipole moment.

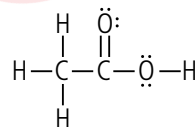
15. The relative tendency of a bonded atom to attract the shared electron pair towards itself is called electronegativity while electron gain enthalpy is the energy change that occurs for the process of adding an electron to a gaseous isolated atom to convert it into a negative ion *i.e.*, to form a monovalent anion. Electron gain enthalpy and electronegativity both measure the power of attracting electrons, but electron gain enthalpy is concerned with an isolated gaseous atom while electronegativity is concerned with the atom in combination.

16. In a hetero atomic molecule the shared pair of electrons between the two atoms gets displaced more towards the electronegative atom. The resultant covalent bond is polar covalent bond. For example, in  $\text{H}-\text{F}$  the electron pair is displaced towards fluorine due to highly electronegative F atom. Hence H develops a partial +ve charge while F develops a partial -ve charge,  $\overset{\delta+}{\text{H}}-\overset{\delta-}{\text{F}}$ .

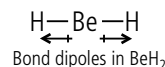
17. As per Fajan's rule,  $\text{N}_2 < \text{SO}_2 < \text{ClF}_3 < \text{K}_2\text{O} < \text{LiF}$

18. In the given figure, hydrogen has valency of two, which is not possible and also octet of oxygen is not complete.

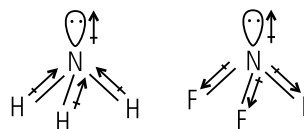
So, the correct structure is



19. The dipole moment in case of  $\text{BeH}_2$  is zero. This is because the two equal bond dipoles point in opposite directions and cancel the effect of each other.



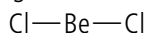
20. Both the molecules  $\text{NH}_3$  and  $\text{NF}_3$  have pyramidal shape with a lone pair of electrons on nitrogen atom. Although fluorine is more electronegative than nitrogen, the resultant dipole moment of  $\text{NH}_3$  ( $4.90 \times 10^{-30} \text{ C m}$ ) is greater than that of  $\text{NF}_3$  ( $0.8 \times 10^{-30} \text{ C m}$ ). This is because, in case of  $\text{NH}_3$  the orbital dipole due to lone pair is in the same direction as the resultant dipole moment of the  $\text{N}-\text{H}$  bonds whereas in  $\text{NF}_3$  the orbital dipole is in the direction opposite to the resultant dipole moment of the three  $\text{N}-\text{F}$  bonds. The orbital dipole because of lone pair decreases the effect of the resultant  $\text{N}-\text{F}$  bond moment which results in low dipole moment of  $\text{NF}_3$  as represented below :



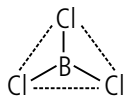
## Topic 2

1. According to VSEPR theory, the shape of molecule depends upon the number of valence shell electron pairs (bonded or non bonded) around the central atom.

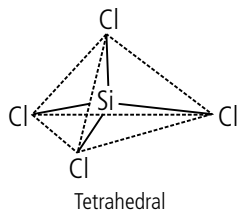
(i) **BeCl<sub>2</sub>** : Presence of two bond pairs and lack of lone pairs gives it a linear shape.



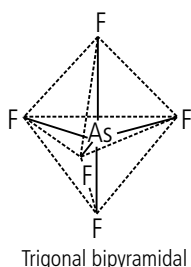
(ii) **BCl<sub>3</sub>** : Presence of three bond pairs and lack of lone pairs gives it trigonal planar geometry.



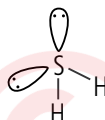
(iii) **SiCl<sub>4</sub>** : Presence of four bond pairs and lack of lone pairs gives it tetrahedral geometry.



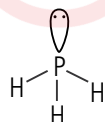
(iv) **AsF<sub>5</sub>** : Presence of five bond pairs and lack of lone pairs gives it trigonal bipyramidal geometry.



(v) **H<sub>2</sub>S** : Presence of two bond pairs and two lone pairs gives it angular or bent shape.



(vi) **PH<sub>3</sub>** : Presence of three bond pairs and one lone pair gives it trigonal pyramidal shape.



2. Bond angle in NH<sub>3</sub> is 107.5° and in H<sub>2</sub>O, angle is 104.5°. In H<sub>2</sub>O, oxygen has two lone pairs and in NH<sub>3</sub>, nitrogen has only one lone pair. In H<sub>2</sub>O, two lone pairs on oxygen repel each other and the bonded pairs more strongly and cause them to come closer thereby reducing the angle.

3. In CH<sub>4</sub>, only bond pairs are there and no lone pairs are present so, to attain most stabilized structure it arranges itself in tetrahedral geometry with greater bond angle of 109° rather than in square planar geometry with lesser bond angle of 90°.

4. Hybridisation can be defined as the process of intermixing of the orbitals of slightly different energies so as to redistribute their energies, resulting in the formation of new set of orbitals of equivalent energies and shape.

**Salient features of hybridisation** : The main features of hybridisation are as under :

- (i) The number of hybrid orbitals is equal to the number of the atomic orbitals that undergo hybridisation.
- (ii) The hybrid orbitals are always equivalent in energy and shape.
- (iii) The hybrid orbitals are more effective in forming stable bonds than the pure atomic orbitals.
- (iv) These hybrid orbitals are directed in space in some preferred directions to have minimum repulsion between electron pairs and thus have a stable arrangement. Therefore, the type of hybridisation indicates the geometry of the molecules.

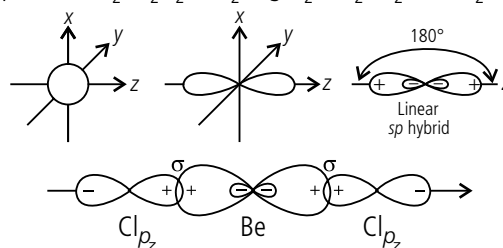
**Important conditions for hybridisation** :

- (i) Only those orbitals that are present in the valence shell of the atom undergo hybridisation.
- (ii) The orbitals undergoing hybridisation should have almost equal energy.
- (iii) Promotion of electron is not essential condition prior to hybridisation.
- (iv) It is not necessary that only half filled orbitals participate in hybridisation. In some cases, even filled orbitals of valence shell take part in hybridisation.

**Shapes of hybrid orbitals** :

(i) **sp-hybridisation** : One 's' and one 'p' orbital of an atom intermix giving two sp-hybrid orbitals making an angle of 180° with each other. Each hybrid orbital has 50% s and 50% p-orbital character. The molecules having such type of hybridisation in their central atom have linear geometry with bond angles 180°.

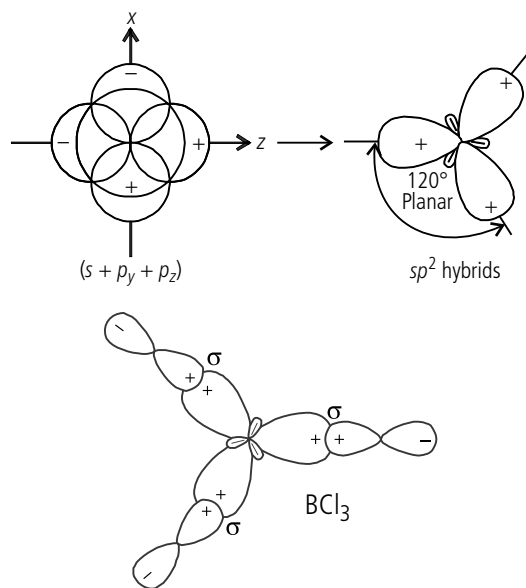
Examples : BeCl<sub>2</sub>, C<sub>2</sub>H<sub>2</sub>, CO<sub>2</sub>, HgCl<sub>2</sub>, CS<sub>2</sub>, N<sub>2</sub>O, BeH<sub>2</sub>, etc.



Formation of sp hybrids from s and p orbitals and formation of the linear BeCl<sub>2</sub> molecule

(ii) **sp<sup>2</sup>-hybridisation** : One 's' and two 'p' orbitals of an atom intermix giving three sp<sup>2</sup>-hybrid orbitals, which are directed towards the corners of an equilateral triangle making an angle of 120° with each other. Each hybrid orbital has 33.3% s and 66.7% p-orbital character. The molecules having

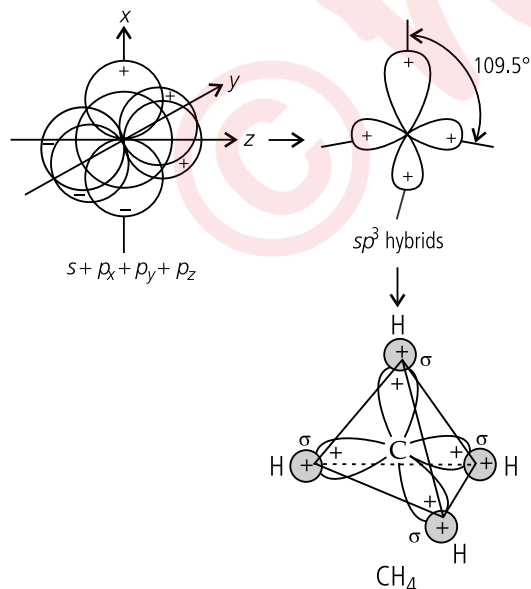
such type of hybridisation in their central atom are expected to have triangular planar geometry with bond angles  $120^\circ$ . Examples :  $\text{BCl}_3$ ,  $\text{BF}_3$ ,  $\text{SO}_3$ ,  $\text{C}_2\text{H}_4$ , Graphite,  $\text{SO}_2$ , etc.



Formation of  $sp^2$  hybrids and the  $\text{BCl}_3$  molecule

(iii)  **$sp^3$ -hybridisation** : One 's' and three 'p' orbitals of an atom intermix giving four  $sp^3$ -hybrid orbitals, which are directed towards the corners of a regular tetrahedron making an angle of  $109^\circ 28'$ . Each hybrid orbital has 25% s- and 75% p-orbital character. The molecules having such type of hybridisation in their central atom are expected to have tetrahedral geometry with bond angles  $109^\circ 28'$ .

Examples :  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{CCl}_4$ ,  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ , diamond, etc.



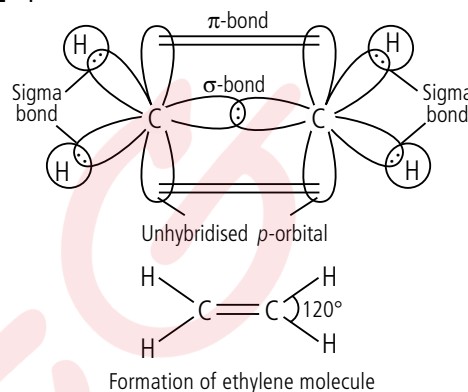
Formation of  $sp^3$  hybrids by the combination of  $s$ ,  $p_x$ ,  $p_y$  and  $p_z$  atomic orbitals of carbon and the formation of  $\text{CH}_4$  molecule

5. There is change in hybridisation from  $sp^2 \rightarrow sp^3$ . In  $\text{AlCl}_3$ , Al is  $sp^2$  hybridised.  $\text{AlCl}_3$  thus has three  $sp^2$  hybrid orbitals

and a vacant unhybrid  $p$ -orbital. When  $\text{AlCl}_4^-$  is formed, Al undergoes  $sp^3$  hybridisation and thus  $\text{Cl}^-$  overlaps with the fourth orbital.

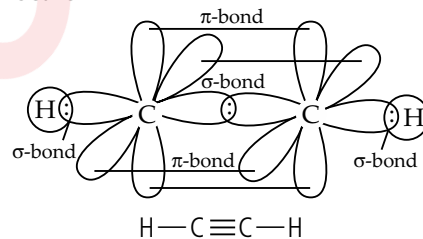
6. In  $\text{BF}_3$ , B is  $sp^2$  hybridised and has one vacant  $p$ -orbital which gets filled by accepting a lone pair of electrons present on the N-atom of  $\text{NH}_3$ . Nitrogen in this adduct acts as donor atom and  $\text{BF}_3$  acts as an acceptor. So, hybridisation of B in  $\text{BF}_3$  changes from  $sp^2$  to  $sp^3$  whereas there is no change in hybridisation of N in  $\text{NH}_3$  and in the adduct.

7.  **$\text{C}_2\text{H}_4$  molecule :**



Formation of ethylene molecule

**$\text{C}_2\text{H}_2$  molecule :**



Formation of acetylene molecule

8. (a)  $\text{C}_2\text{H}_2 \rightarrow \text{H} \overset{\sigma}{\text{C}} \overset{\pi}{\equiv} \overset{\pi}{\text{C}} \overset{\sigma}{\text{H}}$ ;

No. of  $\sigma$  bonds = 3, No. of  $\pi$  bonds = 2

(b)  $\text{C}_2\text{H}_4 \rightarrow \text{H} \overset{\sigma}{\text{C}} \overset{\pi}{=} \overset{\pi}{\text{C}} \overset{\sigma}{\text{H}}$ ; No. of  $\sigma$  bonds = 5,

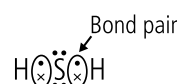
No. of  $\pi$  bond = 1

9. (c) A bond formed between two atoms by the overlap of singly occupied orbitals along their axes (end to end overlap) is called  $\sigma$  bond. Hence,  $1s$  and  $1s$ ,  $1s$  and  $2p_x$  and  $1s$  and  $2s$  will form  $\sigma$  bonds.

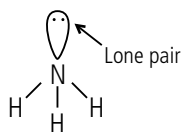
$\pi$  bonds are formed by the sidewise or lateral overlapping of  $p$ -orbitals. Hence,  $p_y$  and  $p_y$  orbitals will form  $\pi$  bond.

10. (a)  $sp^3$ ,  $sp^3$  (b)  $sp^3$ ,  $sp^2$ ,  $sp^2$  (c)  $sp^3$ ,  $sp^3$  (d)  $sp^3$ ,  $sp^2$  (e)  $sp^3$ ,  $sp^2$

11. Bond pairs are the pairs of electrons taking part in bonding, e.g.,



A pair of electrons in a molecule which is not shared by any of the two constituent atoms *i.e.*, does not take part in the direct bonding is called a lone pair, *e.g.*,



## 12. Comparison between $\sigma$ and $\pi$ bonds :

	<b>Sigma bond</b>	<b>Pi bond</b>
1.	The bond is formed by the overlap of orbitals along their axes (end to end overlap). It includes $s-s$ and $p-p$ overlapping.	The bond is formed by sidewise overlapping of orbitals (lateral overlapping). It includes $p-p$ overlapping.
2.	It is a strong bond.	It is a weak bond.
3.	There can be free rotation of atoms around this bond.	Free rotation is not possible around this bond.
4.	The shape of the molecule is determined by these bonds.	These bonds do not affect the shape of the molecule.
5.	$\sigma$ -electrons are referred to as localized electrons.	$\pi$ -electrons are referred to as mobile electrons.

**13.** We can consider two hydrogen atoms  $A$  and  $B$  approaching each other having nuclei  $N_A$  and  $N_B$  and electrons present in them are represented by  $e_A$  and  $e_B$ . When the two atoms are at large distance from each other, there is no interaction between them. As these two atoms begin to approach each other, new attractive and repulsive forces begin to operate.

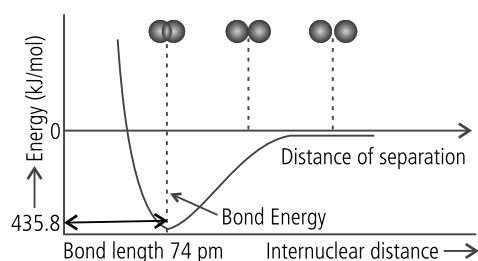
Attractive forces arise between :

- nucleus of one atom and its own electron *i.e.*,  $N_A - e_A$  and  $N_B - e_B$ .
- nucleus of one atom and electron of other atom *i.e.*,  $N_A - e_B$ ,  $N_B - e_A$ .

Similarly repulsive forces arise between :

- electrons of two atoms *i.e.*,  $e_A - e_B$ .
- nuclei of two atoms *i.e.*,  $N_A - N_B$ .

Attractive forces tend to bring the two atoms close to each other whereas repulsive forces tend to push them apart.

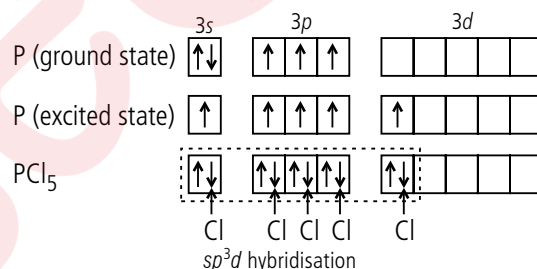


Experimentally it has been found that the magnitude of new attractive forces is more than the new repulsive forces. As a result, two atoms approach each other and potential energy decreases. Ultimately a stage is reached where the net force of attraction balances the force of repulsion and system acquires minimum energy. At this stage two hydrogen atoms are said to be bonded together to form a stable molecule having the bond length of 74 pm.

Since the energy gets released when the bond is formed between two hydrogen atoms, the hydrogen molecule is more stable than isolated hydrogen atoms. The energy so released is called bond enthalpy, which corresponds to the minimum in the curve depicted in fig. Conversely, 435.8 kJ of energy is required to dissociate one mole of  $H_2$  molecule.

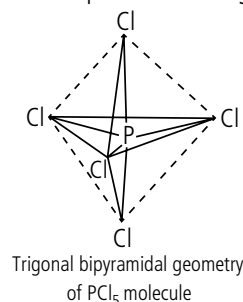


**14. Formation of  $PCl_5$  ( $sp^3d$  hybridisation) :** The ground state and the excited state outer electronic configurations of phosphorus ( $Z = 15$ ) are represented here.



(orbitals filled by electron pairs donated by five Cl atoms.)

Now the five orbitals (*i.e.*, one  $s$ , three  $p$  and one  $d$  orbital) are available for hybridisation to yield a set of five  $sp^3d$  hybrid orbitals which are directed towards the five corners of a trigonal bipyramid as depicted in the figure.



All the bond angles in trigonal bipyramidal geometry are not equivalent. In  $PCl_5$  the five  $sp^3d$  orbitals of phosphorus overlap with the singly occupied  $p$  orbitals of chlorine atoms to form five P-Cl sigma bonds. Three P-Cl bonds lie in one plane and make angle of  $120^\circ$  with each other; these bonds are termed as equatorial bonds. The remaining two P-Cl bonds, one lying above and the other lying below the equatorial plane, make an angle of  $90^\circ$  with the plane. These

bonds are called axial bonds. As the axial bond pairs suffer more repulsive interaction from the equatorial bond pairs, therefore axial bonds have been found to be slightly longer and hence slightly weaker than the equatorial bonds.

### Topic 3

1. Necessary conditions for linear combination of atomic orbitals :

(i) The symmetry and relative energies of combining atomic orbitals  $\psi_A$  and  $\psi_B$  must be close to each other.

(ii) The extent of overlap between the charge clouds of  $\psi_A$  and  $\psi_B$  should be large.

(iii) Atomic orbitals of the same sign should overlap.

2. Beryllium atom has electronic configuration,  $1s^2 2s^2$ . So, in  $\text{Be}_2$  there are a total of eight electrons which must be filled in four molecular orbitals.

M.O. configuration of  $\text{Be}_2 \rightarrow \sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2$

B.O. =  $1/2(4 - 4) = 0$ . Since the bond order is zero it shows that molecular beryllium will not exist.

3.

Species	Total electrons	Configuration	Bond order	Magnetic character
$\text{O}_2$	16	$KK\sigma(2s)^2 \sigma^*(2s)^2 \sigma(2p_z)^2 \pi(2p_x)^2 = \pi(2p_y)^2$ $\pi^*(2p_x)^1 = \pi^*(2p_y)^1$	$\frac{(8-4)}{2} = 2.0$	Paramagnetic
$\text{O}_2^+$	15	$KK\sigma(2s)^2 \sigma^*(2s)^2 \sigma(2p_z)^2 \pi(2p_x)^2 = \pi(2p_y)^2$ $\pi^*(2p_x)^1$	$\frac{(8-3)}{2} = 2.5$	Paramagnetic
$\text{O}_2^-$	17	$KK\sigma(2s)^2 \sigma^*(2s)^2 \sigma(2p_z)^2 \pi(2p_x)^2 = \pi(2p_y)^2$ $\pi^*(2p_x)^2 = \pi^*(2p_y)^1$	$\frac{(8-5)}{2} = 1.5$	Paramagnetic
$\text{O}_2^{2-}$	18	$KK\sigma(2s)^2 \sigma^*(2s)^2 \sigma(2p_z)^2 \pi(2p_x)^2 = \pi(2p_y)^2$ $\pi^*(2p_x)^2 = \pi^*(2p_y)^2$	$\frac{(8-6)}{2} = 1.0$	Diamagnetic

$\therefore$  Higher the bond order, higher is the stability. Relative order of stability is  $\text{O}_2^+ > \text{O}_2 > \text{O}_2^- > \text{O}_2^{2-}$ .

4. The plus and minus sign indicate the sign of the wave function in the various lobes and not that of the nuclear or electronic charges. The '+' sign (or upward crest) represents one phase and the '-' sign represents second phase of the wave function. Bonding molecular orbital is formed by combination of '+' with '+' and '-' with '-' part of the electron waves whereas antibonding molecular orbital is formed by combination of '+' with '-' part of the electron waves.

As orbitals are represented by wave functions, a plus sign in an orbital represents a +ve wave function and a minus sign represents a -ve wave function.

5. Hydrogen bond can be defined as an attractive force which binds hydrogen atom of one molecule with the electronegative atom (F, O or N) of another molecule. Following conditions should be fulfilled by a molecule for the formation of hydrogen bond :

(a) Hydrogen atom should be linked to a highly electronegative atom, such as F, O or N through a covalent bond.

(b) The size of the electronegative atom bonded covalently to the hydrogen atom should be small.

Hydrogen bond is stronger than van der waals' forces.

6. Bond order of a molecule or an ion is a measure of the strength or stability of the bond. Numerically, it is half of the difference between number of electrons in bonding ( $N_b$ ) and

in anti-bonding ( $N_a$ ) molecular orbitals.

$$\text{Bond order} = \frac{1}{2}(N_b - N_a)$$

If B.O. is zero or negative, the bond is highly unstable *i.e.*, the molecule does not exist. Higher bond order means high bond dissociation energy and greater stability. Greater the bond order, lesser is the bond length.

M.O. configuration of  $\text{N}_2$  :

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

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

M.O. configuration of  $\text{O}_2$  :

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

$$\pi^*(2p_x)^1 = \pi^*(2p_y)^1$$

$$\text{Bond order} = \frac{(8-4)}{2} = 2$$

M.O. configuration of  $\text{O}_2^+$  :

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

$$\text{Bond order} = \frac{(8-3)}{2} = 2.5$$

M.O. configuration of  $\text{O}_2^-$  :

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

$$= \pi^*(2p_y)^1$$

$$\text{Bond order} = \frac{(8-5)}{2} = 1.5$$



