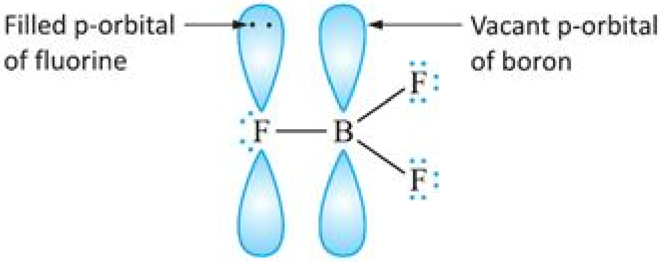
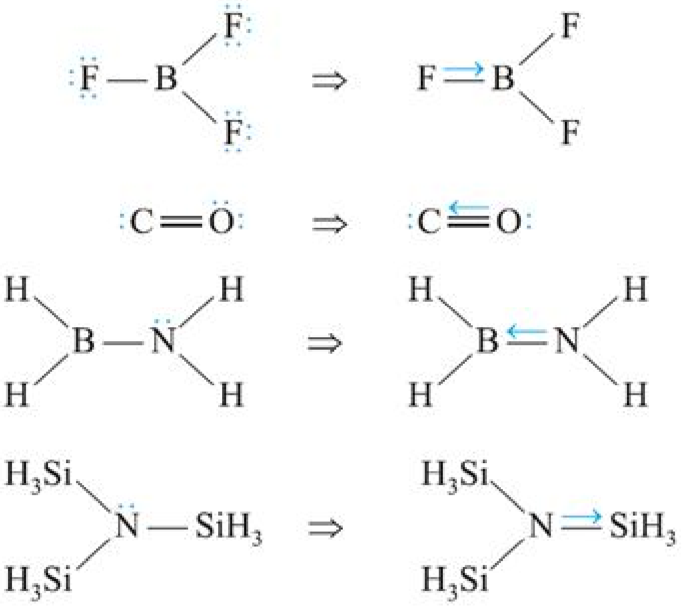
Chemical Bonding - II

Till now we have learnt about the various aspects of chemical bonding. In this part of the chapter we will try to summarize the method to find shapes and hybridisation of molecules and will also learn about Molecular Orbital Theory.

BACK BONDING Section - 1

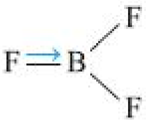
Back (π) bond is a co-ordinate bond formed between electron rich atom (donor) and neighbouring electron deficient atom or atom having vacant orbital (acceptor) of a molecular species. For example in BF_3 back bonding is due to by donation of an electron pair from filled orbital of fluorine atom to vacant p-orbital of boron.



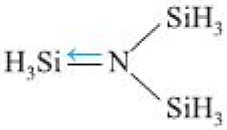


This back (π) bonding may results in change in hybridization state, molecular geometry, bond angle, bond strength and Lewis basic strength. For example in $N(SiH_3)_3$ hybridization state of nitrogen atom is sp^2 and it is not a Lewis base.

Further this back (π) bonding can be Pπ–Pπ and Pπ–dπ type depending upon type of filled orbital and vacant orbital. For example:



Pπ-Pπ Back bonding



Pπ-dπ Back bonding

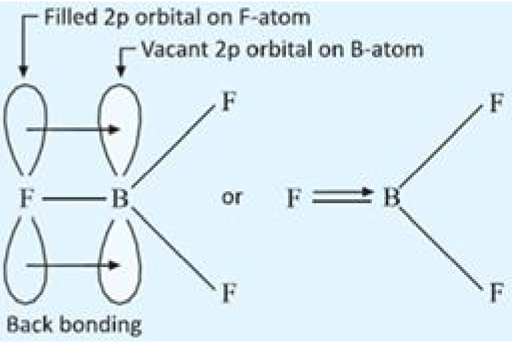
Illustration - 1 *Account for the fact that Lewis acid character of BF_3, BCl_3 and BBr_3 increases as $BF_3 < BCl_3 < BBr_3$.*

SOLUTION:

The increasing order of Lewis acid strength (or character) ($BF_3 < BCl_3 < BBr_3$) can be explained on the basis of the concept of ($p\pi$–$p\pi$) back bonding that takes place in given halides.

We know that in each of the given trihalide molecules B-atom is sp^2 hybridised and has one unused vacant $2p$ orbital. Each of the three halogen atoms in each BX_3 molecule (X : F, Cl, Br) has three pairs of electrons which are present in s and p-orbitals respectively (F = $2s^2\ 2p^2\ 2p^2\ 2p^1$; Cl = $3s^2\ 3p^2\ 3p^1$; Br = $4s^2\ 4p^2\ 4p^2\ 4p^1$). p–orbital having unpaired electron is used up in forming B–X bond in BX_3 molecule by overlapping with singly-filled sp^2 hybrid orbital of B–atom.

In BF_3 molecule, vacant $2p$ orbital on B–atom an fully-filled $2p$ orbital of F–atom overlap sidewise to form (F→B) π–bond which is called dative or ($p\pi$–$p\pi$) bonding It is due to ($p\pi$–$p\pi$) back bonding that B–F bond acquire some double bond character.



Formation of $p\pi$–$p\pi$ back bonding in one of the three B–F bonds in BF_3.

Back bonding in BF_3 molecule is supported by the fact that the observed B–F bond length in BF_3 which is equal to 1.30 $\mathring{A}$ is significantly shorter than the sum of the covalent radii of B and F atoms (B = 0.80 $\mathring{A}$, F = 0.72 $\mathring{A}$, Sum = 0.80 +0.72 = 1.52 $\mathring{A}$).

The formation of ($p\pi$–$p\pi$) bond results in that the electron pair is transfered from F–atom to the electron deficient B–atom and hence electron density on B–atom in BF_3 molecule is increased or the tendency of B–atom to accept the electron pair is decreased, i.e. the Lewis acid strength of BF_3 molecule, according to lewis concept, is also decreased.

We have seen above that ($p\pi$–$p\pi$) back bonding in BF_3 molecule result from [$2p^2$(F)–$2p^0$(B)] sidewise overlap, but the same in BCl_3 and BBr_3 molecules is obtained by [$3p^2$(Cl)–$2p^0$(B)] and [$4p^2$(Br)–$2p^0$(B)] sidewise overlaps respectively.

Now since the energy and shape of two $2p$ orbitals (one $2p$ orbital on B–atom an one $2p$ orbital on F-atom) involved in [$2p^2$(F)–$2p^0$(B)] overlap to from ($p\pi$–$p\pi$) bonding in BF_3 molecule is the same, this overlap is symmetrical and hence is the most effective. Consequently the transfer of electron pair from $2p$ orbital of F–atom to the vacant $2p$ orbital of B–atom takes place to the maximum extent and hence maximum electron density developed on B–atom in BF_3 molecule. Due to maximum electron density developed on B-atom in BF_3 molecule, this molecule shows minimum tendency to accept electron pair donated by a Lewis base (electron pair donor species) and hence is the weakest Lewis acid. On the other hand, since the energy and shape of 4*p* orbital of Br atom and 2*p* orbital of B-atom involved in [$4p^2$ (Br)–$2p^0$ (B)] overlap in BBr_3 molecule is largely different, this overlap is unsymmetrical and hence is the least effective.

Consequently the transfer of electron pair from 4*p* orbital of Br–atom to the vacant 2*p* orbital of B-atom takes place to the minimum extent and hence minimum electron density is developed on B–atom in BBr_3 molecule. Due to minimum electron density developed on B–atom, BBr_3 molecule shows maximum tendency to accept electron pair donated by a Lewis base and hence is the strongest Lewis acid.

Above discussion shows that the tendency to form ($p\pi$–$p\pi$) back bonding decreases rapidly as we move from BF_3 to BBr_3 and hence the tendency of BF_3, BCl_3 and BBr_3 molecules to accept electron pair from Lewis bases increases in the same direction, i.e. Lewis acid strength (or character) increases as $BF_3 < BCl_3 < BBr_3$.

Illustration - 2 *($p\pi$–$p\pi$) back bonding occurs in the halides of boron but not in those of aluminium. Explain.*

SOLUTION :

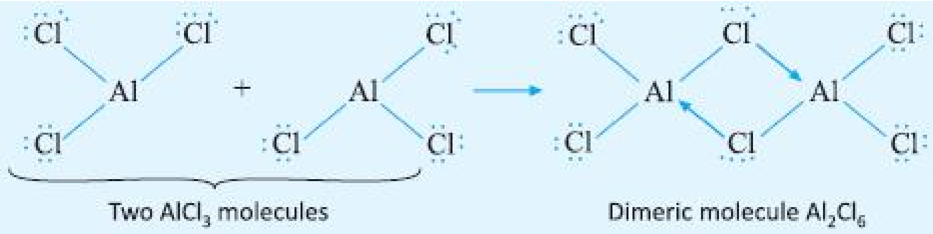
The tendency of the central atom (A) in AX_3 molecules (A = B or Al, X = halogen) to from ($p\pi$–$p\pi$) back bonding depends on the size of the central atom (A). Smaller is the size of the central atom, greater is its tendency to form ($p\pi$–$p\pi$) back bonding. Since B–atom is smaller in size than Al–atom, BX_3 molecules have ($p\pi$–$p\pi$) back bonding while AlX_3 molecules do not have this type of back bonding.

Illustration - 3 *Explain why $AlCl_3$ exists as a dimer, $(AlCl_3)_2$ or Al_2Cl_6 while BCl_3 exits as a monomer.*

OR *Explain the formation of dimeric structure of $AlCl_3$ in benzene (inert solvent) and in the vapour state.*

OR *Explain why all Al-Cl bonds in Al_2Cl_6 are not equivalent.*

SOLUTION :



In $AlCl_3$ molecule, Al-atom is surrounded by six electrons which are less by two electrons from an octet. In dimeric structure (Al_2Cl_6), Al–atom of both $AlCl_3$ molecules completes its octet by accepting an electron pair from Cl-atom of the other $AlCl_3$ molecule as shown. Thus we see that in Al_2Cl_6 dimer each Al-atom is holding four large-sized Cl-atoms around it.

Since B-atom is very small in size, this atom is not capable of holding four large-sized Cl-atoms around it in B_2Cl_6 molecule and hence BCl_3 molecule cannot dimerise to form dimeric molecule, $(BCl_3)_2$ or B_2Cl_6.

The formation of dimeric molecule, Al_2Cl_6 can be explained on the basic of hybridisation concept as follows. We know that in $AlCl_3$ molecule Al-atom (Al = $3s^1\,3p^1\,3p^1\,3p^0$) is sp^2 hybridised and one 3*p* orbital remains vacant and unhybridised. In $AlCl_3$ molecule Al has coordination number equal to 3. In the formation of Al_2Cl_6, the vacant and unhybridised 3*p* orbital on Al-atom of one $AlCl_3$ molecule receives a lone pair of electrons from 3*p* orbital of Cl-atom (Cl = $3s^2\,3p^2\,3p^2\,3p^1$) of the other $AlCl_3$ molecule and thus forms a $[3p^2\,(Cl) \longrightarrow 3p^0\,(Al)]$ coordinate bond. In this way each Al-atom completes its octet and coordination number of Al-atom is increased from 3 (in $AlCl_3$) to 4 (Al_2Cl_6). Thus we see that two bridges are formed by two Cl-atoms between two Al-atoms.

The structure of Al_2Cl_6 has six Al-Cl covalent bonds and two $Cl \longrightarrow Al$ coordinate bonds, these bonds donot have equal length, i.e. all Al-Cl bonds in Al_2Cl_6 are not equivalent.

APPLICATION OF DIPOLE MOMENT Section - 2

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

(ii) To determine percentage of ionic charcter : The value of dipole moment can be used for determining the amount of ionic character in a bond.

$$\mu = q \times d$$

Consier a diatomic molecules say HCl. Suppose this molecule is completely ionic. Under this condition H^+ and Cl^- ions would bear a unit charge equal to 4.8×10^{-10} esu and the bond distance between H and Cl atoms = 1.27 Å.

Thus, theoretical value of $\mu = 4.8 \times 10^{-10} \times 1.27 \times 10^{-8} = 6.09$ D

Dipole moment of HCl is also determined experimentally. Let the experimental value be 1.03 D. Percentage of ionic character in H—Cl bond in HCl molecule $= \dfrac{\text{Experimental value of } \mu}{\text{Theoretical valueof } \mu} \times 100 = \dfrac{1.03}{6.09} \times 100 = 16.9\%$

Thus, $\boxed{\text{percentage of ionic character} = \dfrac{\text{Experimental value of dipole moment}}{\text{Theoretical value of dipole moment}} \times 100}$

(iii) To determine geometry of molecules : The values of dipole moments provide value information about the structure of molecules.

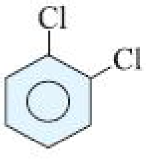
(a) CO_2, CS_2 molecules are linear as value of their dipole moments are zero.

(b) H_2O is not a linear molecule as it has dipole moment. Actually, it has V-shaped structure and the bond angle is 105°. Similary, SO_2 has a bent structure.

(c) In ammonia, three hydrogen atoms do not lie symmetrically with respect to nitrogen as it has dipole moment. It has pyramidal structure.

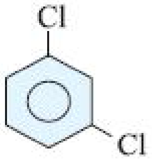
(iv) **To determine orientation in benzene ring :** Dipole moment is useful to ascertain the orientation of substituents. In general, dipole moment follows the order :

Ortho-isomer > meta-isomer > p-isomer



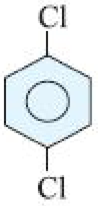
Ortho

$\mu = 2.54$ D



Meta

$\mu = 1.48$ D



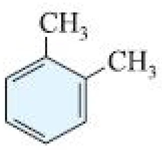
Para

$\mu = 0$

Observe that :

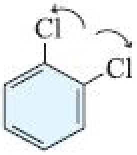
$$\mu_o > \mu_m > \mu_p$$

In ortho isomers, experimental value of dipole moment is found different from theoretical value of dipole moment. This difference is due to dipole-dipole interaction of two groups.



$\mu_{exp} = \mu_{theo}$

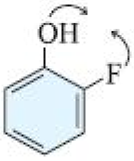
(No interactions between two group)



$\mu_{exp} < \mu_{theo}$

(Repulsion)

(θ increase, μ decreases)



$\mu_{exp} > \mu_{theo}$

(Attraction due to H-bond)

(θ decreases, μ increases)

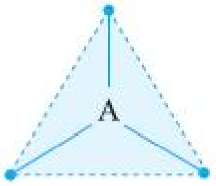
(v) **Bond moment :** The contribution of individual bond in the dipole moment of a polyatomic molecule is termed bond moment. The measured dipole moment of water molecule is 1.85 D. This dipole moment is the vectorial sum of the individual bond moments of two O — H bond having bond angle 104.5°.

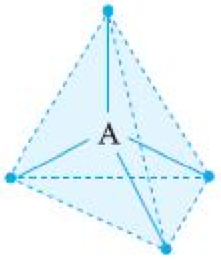
Thus, $\mu_{obs} = 2\mu_{O-H} \cos 52.25$

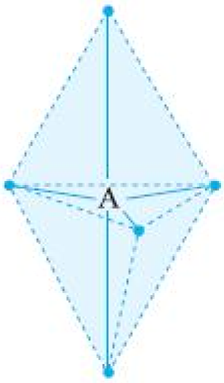
$$1.85 = 2\mu_{O-H} \times 0.6129$$

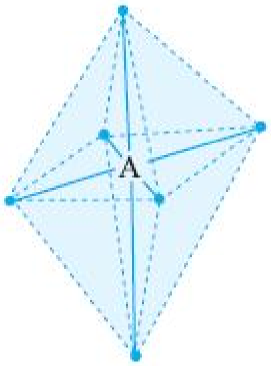
$$\mu_{O-H} = 1.51 \text{ D}$$

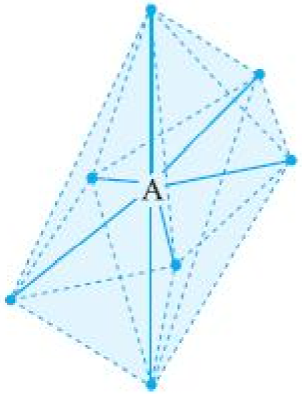
PREDICTION OF GEOMETRY (SHAPE) OF COVALENT MOLECULES Section - 3











Geometry of a molecule can be predicted if the state of hybridization at central atom is known. State of hybridization at central atom in a molecule can be known by counting the number of orbitals involved in co-axial overlapping and the number of orbitals with lone pair of electons, i.e., by counting the number of σ-bonds and the number of lone pair of electrons at central atom. Adding the two if total is 4, the hybridization is sp^3, if this total is 3, the hybridization is sp^2 and if this total is 2, the hybridization is sp. A few examples are being given below :

(a) Beryllium chloride ($BeCl_2$)

Outer Electronic Configuration of Be = $2s^2$

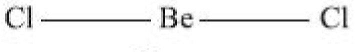
Since there are two chlorine atoms, hence Beryllium must be forming a single bond with each of them (as chlorine has a valency equal to 1).

- This implies that before bonding there should be two orbitals around Beryllium having exactly one electron in each of them so that they are available for overlapping with the respective orbitals of the chlorine atoms.
- Thus we excite one of the electrons present in 2*s* orbital to 2*p* orbital to generate two singly occupied orbitals.
- Outer Electronic Configuration of Be (after excitation of electrons) = $2s^1\ 2p^1$.

- Now before bonding 2*s* and 2*p* orbital hybridize to produce two sp orbitals of same energy and same shape which overlap with p orbital of incoming chlorine atom to form two sigma bonds.
- Number of σ-bonds (bond pairs) at Be atom = 2 and

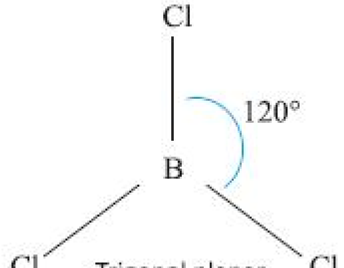
  Number of lone pair of electrons at Be atom = 0 , Total number of electron pairs = 2 + 0 = 2

  Hybridization is *sp*, i.e., $BeCl_2$ is linear and bond angle is 180°.



Linear

(b) Boron trichloride (BCl_3)



Trigonal planar

Boron is forming three bonds with three chlorine atoms.

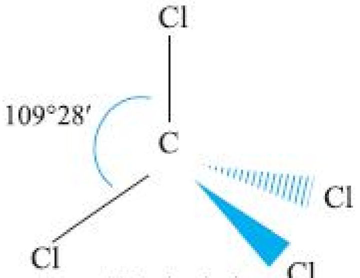
Outer Electronic Configuration of B = $2s^2\,2p^1$

- Outer Electronic Configuration of B (after excitation of electrons) = $2s^1\,2p_x^{\,1}\,2p_y^{\,1}$
- Number of σ-bonds (bond pairs) at B atom = 3

  Number of lone pair of electrons at B atom = 0, Total number of electron pairs = 3

  Hybridization is sp^2, i.e., BCl_3 is trigonal planar and bond angles are 120° each.

(c) Carbon tetrachloride (CCl_4)



Tetrahedral

Carbon is forming four bonds with four Chlorine atoms.

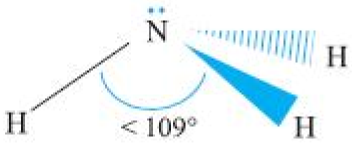
Outer Electronic Configuration of C = $2s^2\,2p^2$

- Outer Electronic Configuration of C (after excitation of electrons) = $2s^1\,2p_x^{\,1}\,2p_y^{\,1}\,2p_z^{\,1}$
- Number of σ-bonds (bond pairs) at C atom = 4

  Number of lone pair of electrons at C atom = 0, Total number of electron pairs = 4

  Hybridization is sp^3, i.e., CCl_4 is tetrahedral and bond angles are 109°28′ each.

(d) Ammonia (NH_3)



Trigonal pyramidal

Nitrogen is forming three bonds with three hydrogen atoms.

Outer Electronic Configuration of N = $2s^2\,2p^3$

- Outer Electronic Configuration of N (before bonding) = $2s^2\,2p_x^{\,1}\,2p_y^{\,1}\,2p_z^{\,1}$
- Number σ-bonds (bond pairs) at N atom = 3

Number of lone pair of electrons at N atom = 1, Total number of electron pairs = 3 + 1 = 4

Hybridization is sp^3 and geometry of NH_3 molecule is tetrahedral, however the shape is trigonal pyramidal and bond angles are not 109°28′ but 106°45′.

(e) Water (H_2O)

V-shaped (bent)

Oxygen is forming two bonds with two hydrogen atoms.

Outer Electronic Configuration of O = $2s^2\,2p^4$

- Outer Electronic Configuration of C (before bonding) = $2s^2\ 2p_x^{\ 2}\ 2p_y^{\ 1}\ 2p_z^{\ 1}$
- Number of σ-bonds (bond pairs) at O atom = 2

Number of lone pair of electrons at O atom = 2 Total number of electron pairs = 2 + 2 = 4

Hybridization is sp^3 and geometry of water molecule is tetrahedral, however the shape is bent and bond angles are not 109°28′ but 104.5°.

Molcecular Shapes

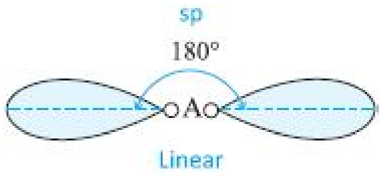
Note : (a) For Column 2 (Type) : Type AB_3L_2 means in this molecule central atom (denoted by A) has three bond pairs (denoted by B_3) and two lone pairs (denoted by L_2) .

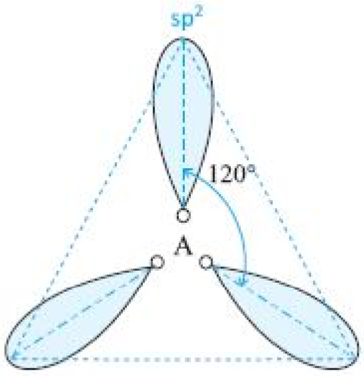
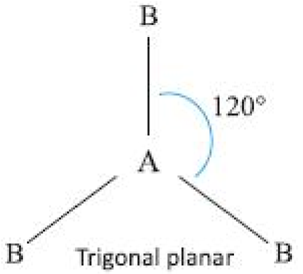
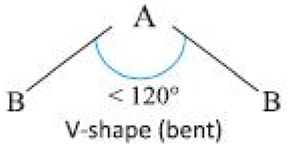
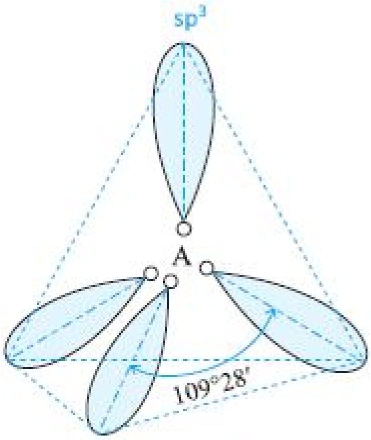
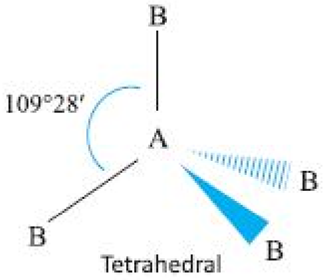
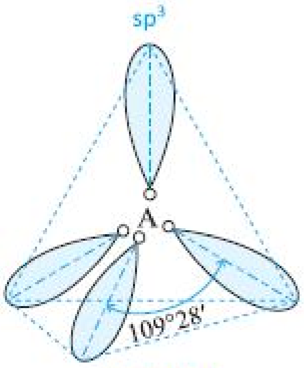
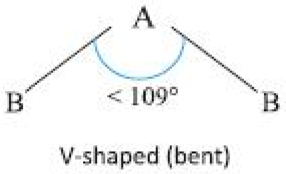
(b) For Column 3 : E = B + L

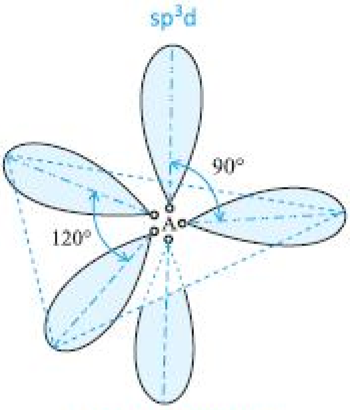
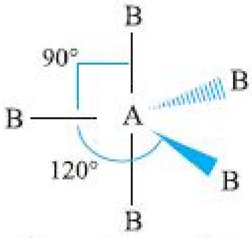
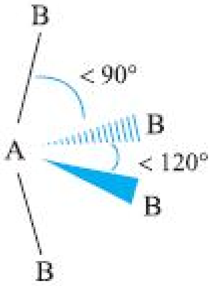
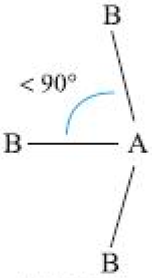
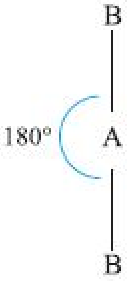
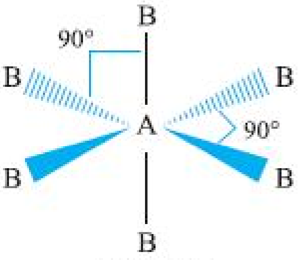
E : stands for total number of electron pairs present in the outer most shell of the central atom.

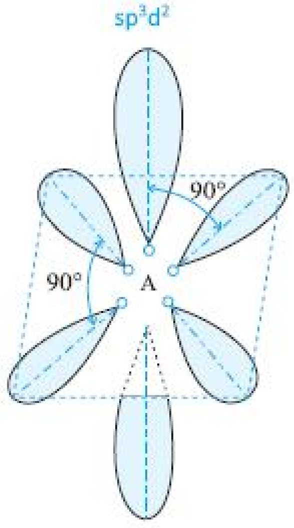
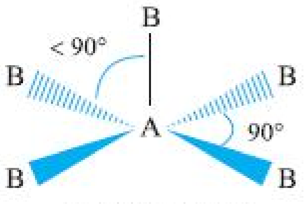
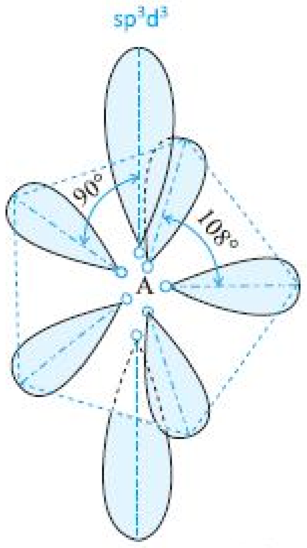
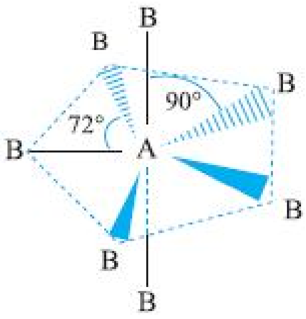
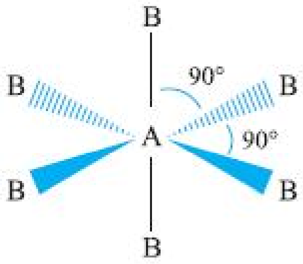
B : stands for the number of bond pairs present around the central atom.

L : stands for the number of lone pairs present around the central atom.

Hybridisation and Geometry of molecules	Type	E(B + L)	Actual shape of molecules	Bond Angle	Examples
	AB_2	2(2 + 0)	B —— A —— B Linear	180°	CO_2, $HgCl_2$, BeF_2, $ZnCl_2$, $MgCl_2$, C_2H_2, HCN, $BeCl_2$
	ABL	2(1+1)	A —— B Linear		N_2, CN^-

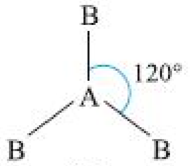
 Trigonal planar	AB_3	$3(3+0)$		120^o	$BF_3, AlCl_3,$ $SO_3, C_2H_4,$ $NO_3^-, CO^{2-},$ $HCHO, C_6H_6$
	AB_2L	$3(2+1)$		$<120^o$	NO_2, SO_2, $SnCl_2$
 Tetrahedral	AB_4	$4(4+0)$		$109^o28'$	$CH_4, SiH_4,$ SO_4^{2-}, $SnCl_4$ ClO_4^-, BF_4^-, NH_4^+
 Tetrahedral	AB_3L	$4(3+1)$		$<109.5^o$	NH_3, PCl_3, PH_3, AsH_3, ClO_3^-, NF_3
	AB_2L_2	$4(2+2)$		$<109.5^o$ $\sim (90^o$ $-104^o)$	H_2O, H_2S, $PbCl_2, OF_2,$ NH_2^-, ClO_2^-

 Trigonal Bipyramidal	AB_5	$5(5+0)$	 Trigonal Bipyramidal	120^o (equatorial) and 90^o (Axial)	PCl_5, $SbCl_5$
	AB_4L	$5(4+1)$	 (Bent) Seesaw, Sawhorse, folded square, (distorted/irregular) Tetrahedral	$<120^o$ and $<90^o$	$TeCl_4$, SF_4, XeO_2F_2, IF_4^+
	AB_3L_2	$5(3+2)$	 T-shaped	$<90^o$	ClF_3, IF_3
	AB_2L_3	$5(2+3)$	 Linear	180^o	I_3^-, XeF_2
	AB_6	$6(6+0)$	 Octahedral	90^o	SF_6, PF_6^-, $SnCl_6^-$

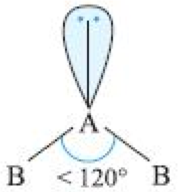
 Octahedral	AB_5L	6(5 + 1)	 Square pyramidal	90^o (equatorial) and $< 90^o$ (axial)	ICl_5, BrF_5 IF_5, $XeOF_4$
	AB_4L_2	6(4 + 2)	 Square planar	90^o	XeF_4, ICl_4^-
 Pentagonal Bipyramidal	AB_7	7(7 + 0)	 Pentagonal bipyramidal	72^o (equatorial) and 90^o (axial)	IF_7
	AB_6L	7(6 + 1)	 Distorted Octahedral	90^o (equatorial) and 90^o (axial)	XeF_6

A summary of possible shapes is given on the next page.

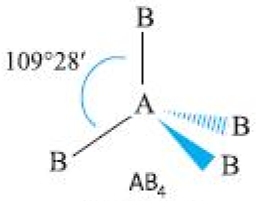
AB_2
Linear



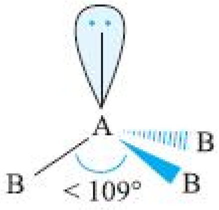
AB_3
Trigonal planar



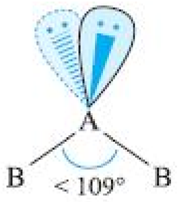
AB_2L_1
Bent or Angular



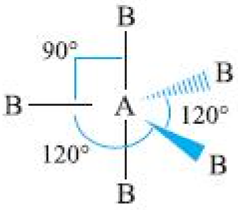
AB_4
Tetrahedral



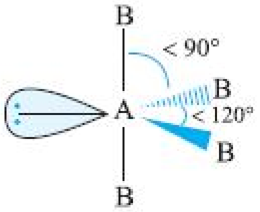
AB_3L_1
Trigonal pyramidal



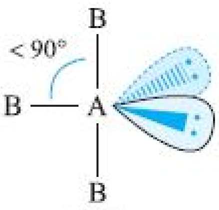
AB_2L_2
Bent or Angular



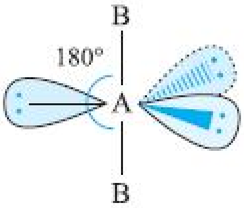
AB_4
Trigonal bipyramidal



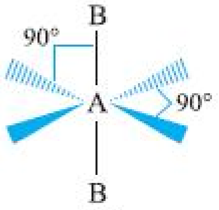
AB_4L_1
Sawhorse or Seesaw



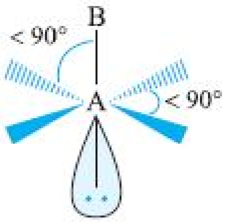
AB_3L_2
T-shape



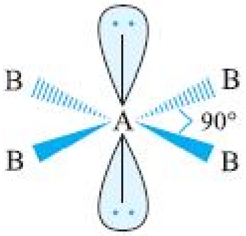
AB_2L_3
Linear



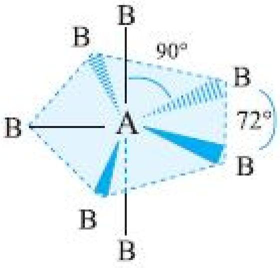
AB_6
Octahedral



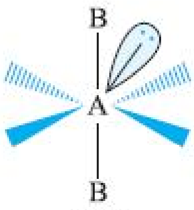
AB_5L_1
Square pyramidal



AB_4L_2
Square planar



AB_7
Pentagonal bipyramidal

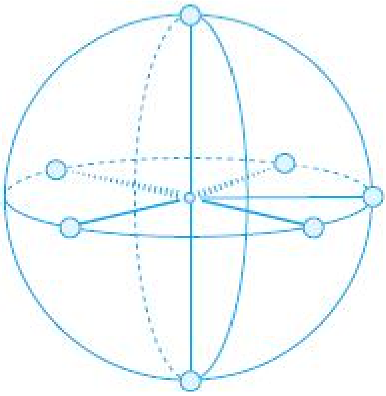


AB_6L

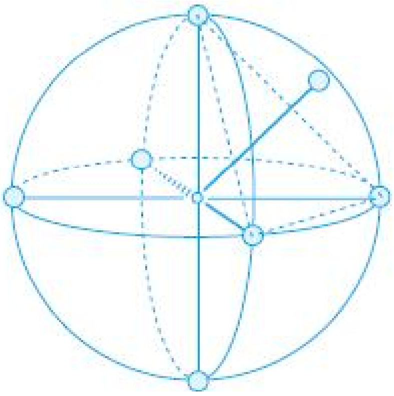
Distorted Octahedral

VSEPR and More than six Electron Pairs

It is considerably less easy to draw a distinction between apparently reasonable seven coordinate geometries. There are several possibilities, including the pentagonal bipyramid and the capped octahedron.



Pentagonal Bipyramid



Monocapped Octahedron

Iodine heptafluoride, IF_7, is a good example of a pentagonal bipyramidal geometry. The molecule XeF_6 is an interesting case. As with IF_7, application of VSEPR rules suggests seven electron pairs, XeF_6 is made up from six bonding pairs and one lone pair. In fact, the structure of XeF_6 is based upon a distorted octahedron, probably towards a monocapped octahedron.

Illustration - 4 *Determine the hybridisation, geometry, number of lone pair, bond pairs in the following compounds.*

$SO_2, SO_3, NH_4^+, IF_4^+, ClF_3, I_3^-, PF_6^-, XeOF_4$

SOLUTION :

(a) Sulphur dioxide (SO_2)

In SO_2 molecule sulphur forms bonds with two oxygen atoms

Outer Eletronic Configuration of O $= 2s^2 2p^4$
$= 2s^2\ 2p_x^2\ 2p_y^1\ 2p_z^1$

Now between any two atoms there can only one sigma (diect) overlap.

⇒ Each oxygen atom will form one sigma bond with the sulphur atom.

⇒ However, to complete its octet of electrons each oxygen atom needs 2 more electrons and hence it needs to form two bonds (or two overlaps).

⇒ Each Oxygen will form another bond with the Sulphur atom by sideways (overlap or π bond).

⇒ Each Oxygen atom forms 1 sigma and 1 pie bond with Sulphur atom.

⇒ Sulphur atom will make 2 sigma and 2 pie bonds with the oxygen atoms.

Outer Eletronic Configuration of S

$= 3s^2\ 3p^4 = 3s^2\ 3p_x^2\ 3p_y^1\ 3p_z^1$

V-shape (bent)
[Trigonal planar]

Since Sulphur will form 2 pie bonds, hence remove two of its outer electrons as they will take part in sideways overlap (to form the pie bond).

⇒ Outer Electronic Configuration of S (with electrons removed) = $3s^2\ 3p_x^{\ 2}$

⇒ Outer Electronic Configuration of S (before bonding) = $3s^2\ 3p_x^{\ 1}\ 3p_y^{\ 1}$

➤ Now before bonding 3*s*, $3p_x$ and $3p_y$ orbitals hybridize to produce three sp^2 orbitals of same energy and same shape, out of which one orbitals has two electrons and two orbitals are singly occupied (one electron each) which overlap with *p* orbitals of incoming Oxygen atoms to form two sigma bonds.

➤ Number of σ-bonds (bond pairs) at S atom = 2

Number of lone pair of electrons at S atom = 1

Total number of electron pairs
= 2 + 1 = 3

Hybridization of sulphur in SO_2 is sp^2 and geometry of the molecule is trigonal planar, however since one of the electron pair, hence its actual shape is bent and the O-S-O bond angle is less than 120° (as *lp*-*bp*) repulsion is more than *bp*-*bp* repulsion).

(b) Sulphur trioxide (SO_3)

In SO_3 molecule, sulphur is bonding with three oxygen atoms.

Outer Electronic Configuration of O

$= 2s^2\ 2p^4$

$= 2s^2\ 2p_x^{\ 2}\ 2p_y^{\ 1}\ 2p_z^{\ 1}$

Each Oxygen atom forms 1 sigma and 1 pie bond with Sulphur atom.

⇒ Sulphur atom will make 3 sigma and 3 pie bonds with oxygen atoms.

Outer Electronic Configuration of S
$= 3s^2\ 3p^4 = 3s^2\ 3p_x^{\ 2}\ 3p_y^{\ 1}\ 3p_z^{\ 1}$

Since Sulphur will form 3 pie bonds, hence remove three of its outer electrons as they will take part in sideways overlap (to form the pie bond).

⇒ Outer Electronic Configuration of S (with electrons removed) = 3s2 $3p_x^{\ 1}$

⇒ Outer Electronic Configuration of S (before bonding) = $3s^1\ 3p_x^{\ 1}\ 3p_y^{\ 1}$

➤ Now before bonding 3*s*, $3p_x$ and $3p_y$ orbitals hybridize to produce three sp^2 orbitals of same energy and same shape, which are singly occupied (one electron each) which overlap with *p* orbitals of incoming Oxygen atoms to form three sigma bonds.

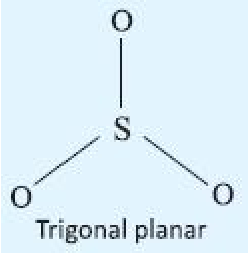
➤ Number of s-bonds (bond pairs) at S atom = 3

Number of lone pair of electrons at S atom = 0

Total number of eletron pairs = 3+ 0 = 3

Hybridization of sulphur is sp^2 and geometry as well as shape of SO_3 is trigonal planar.

of incoming hydrogen atoms to form four sigma bonds.



(c) Ammonium ion (NH_4^+)

In NH_4^+ ion, nitrogen forms four bonds with four hydrogen atoms.

Outer Electronic Configuration of N

$= 2s^2\ 2p^3$

Since there is a positive charge on the ion, hence remove one electron from N.

⇒ Outer Electronic Configuration of N (with electron removed) = $2s^2\ 2p^2$

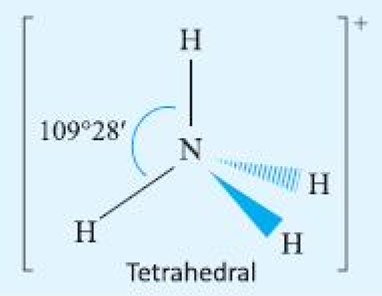
⇒ Outer Electronic Configuration of N (after excitation of electron)
$= 2s^1\ 2p_x^{\ 1}\ 2p_y^{\ 1}\ 2p_z^{\ 1}$

- Now before bonding 2*s*, $2p_x$, $2p_y$ and $2p_z$ orbitals hybridize to produce four sp_3 orbitals of same energy and same shape, which are singly occupied (one electron each) which overlap with s orbitals
- Number of σ-bonds (bond pairs) at N atom = 4

  Number of lone pair of electrons at N atom = 0.

Total number of electron pairs = 4

Hybridization in nitrogen is sp^3 and geometry as well as shape of NH_4^+ is tetrahedral



Tetrahedral

(d) IF_4^+

In IF_4^+ ion, iodine forms four bonds with four flourine atoms.

Outer Electronic Configuration of I = $5s^2\ 5p^5$

Since there is a positive charge on the ion, hence remove one electron from I.

⇒ Outer Electronic Configuration of I (with electron removed) = $5s^2\ 5p^4$

⇒ Electronic Configuration of I (after excitation of electrons)

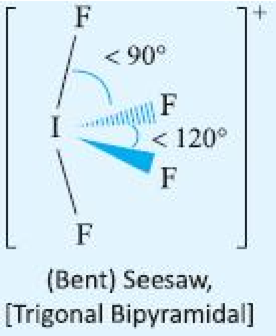
$= 5s^2\ 5p_x^{\ 1}\ 5p_y^{\ 1}\ 5p_z^{\ 1}\ 5d^1$

- Now before bonding 5*s*, $5p_x$, $5p_y$, $5p_z$ and 5*d* orbitals hybridize of produce five sp^3d orbitals of same energy and same shape, out of which one orbital has two electrons and the other four orbitals are singly occupied (one electron each) which overlap with the *p* orbitals of incoming fluorine atoms to form four sigma bonds.
- Number of σ-bonds (bond pairs) at I atom = 4

  Number of lone pair of electrons at I atom = 1

  Those number of electron pairs = 5

Thus hybridisation of iodine is sp^3d and geometry of IF_4^+ is trigonal bipyramidal, however since one of the electron pairs is a lone pair, hence its actual shape is seesaw.



(Bent) Seesaw,
[Trigonal Bipyramidal]

(e) ClF_3

In ClF3 molecule, chlorine forms three bonds with three flourine atoms.

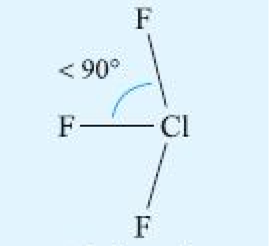
Outer Electronic Configuration of Cl
$= 3s^2\ 3p^5$

- Outer Electronic Configuration of Cl (before bonding
  $= 3s^2\ 3p_x^{\ 2}\ 3p_y^{\ 1}\ 3p_z^{\ 1}\ 3d^1$
- Now before bonding $5s$, $5p_x$, $5p_y$, $5p_z$ and $5d$ orbitals hybridize to produce five sp3d orbitals of same energy and same shape, out of which two orbitals has two electrons and the other three orbitals are singly occupied (one electron each) which oerlap with the p orbitals of incoming fluorine atoms to form three sigma bonds.
- Number s-bonds (bond pairs) at Cl atom = 3

  Number of lone pair of electrons at Cl atom = 2

  Total number of electron pairs
  $= 3 + 2 = 5$

Hybridization of chlorine is sp_3d and geometry of ClF_3 molecule trigonal bipyramidal, however it actually is a T-shaped molecule becuase of the presence of two lone pairs of electrons.



T-shaped
[Trigonal Bipyramidal]

(f) I_3^-

In I_3^- ion, iodine forms two bonds with two other Iodine atoms.

Outer Electronic configuration of I = $5s^2\ 5p^5$

Since there is a negative charge on the ion, hence add one electron in I.

⇒ Outer Electronic Configuration of I (with an electron added) = 5s2 5p6

⇒ Electronic Configuration of I (after excitation of electrons)

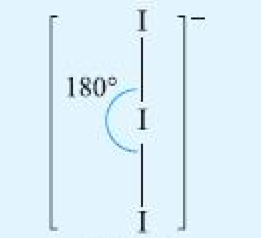
$= 5s^2\ 5p_x^{\ 2}\ 5p_y^{\ 2}\ 5p_z^{\ 1}\ 5d^1$

- Now before bonding $5s$ $5p_x$ $5p_y$ $5p_z$ $5d$ orbitals hybridize to produce five sp^3d orbitals of same energy and same shape, out of which three orbitals have two electrons each and two orbitals are singly occupied which overlap with p orbitals of incoming iodine atoms to form two sigma bonds.
- Number of σ-bonds (bond pairs) at I atom = 2

  Number of lone pair of electrons at I atom = 3

  Total number of electron pairs = 5

Thus hybridization of iodine is sp^3d and geometry of I_3^- ion is trigonal bipyramidal, however its actual shape is a linear because of the presence of three lone pair of electrons.



Linear
[Trigonal Bipyramidal]

(g) PF_6^-

In this ion phosphorous forms six bonds with six flourine atoms.
Outer Electronic Configuration of P = $3s^2\ 3p^3$

Since there is a negative charge on the ion, hence add one electron in P.

⇒ Outer Electronic Configuration of P (with an electron added) = $3s^2\ 3p^4$

⇒ Outer Electronic Configuration of P (after excitation of electrons)

$= 3s^1\ 3p_x^{\ 1}\ 3p_y^{\ 1}\ 3p_z^{\ 1}\ 3d_{xy}^{\ 1}\ 3d_{yz}^{\ 1}$

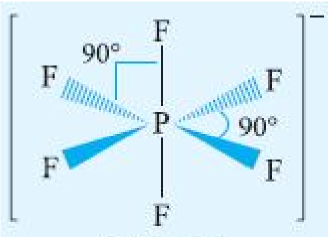
- Now before bonding $3s$, $3p_x$, $3p_y$, $3p_z$, $3d_{xy}$ and $3d_{yz}$ orbitals hybridize to produce six sp^3d^2 orbitals of same energy and same shape, having one

- Number of σ-bonds (bond pairs) at P atom = 6

  Number of lone pair of electrons at P atom = 0

  Total number of electron pairs = 6

Thus hybridisation of PF6- is sp^3d^2 and geometry as well as shape is a Octahedral.



Octahedral

(h) $XeOF_4$

In this molecule xenon forms bonds with one oxygen and four fluorine atoms.

Outer Electronic Configuration of Xe
$= 5s^2\ 5p^6$

$= 5s^2\ 5p_x^{\ 2}\ 5p_y^{\ 2}\ 5p_z^{\ 2}$

The Oxygen atom forms 1 sigma and 1 pie bond with Xenon atom and the four fluorine atoms form 1 sigma bond each with the xenon atom.

⇒ Xenon atom forms 5 sigma bonds and 1 pie bond.

Since Xenon will form 1 pie bond, hence remove one of its outer electrons as they will take part in sideways overlap (to form the pie bond).

⇒ Outer Electronic Configuration of Xe (with an electron removed)

$= 5s^2\ 5p_x^{\ 2}\ 5p_y^{\ 2}\ 5p_z^{\ 1}$

⇒ Outer Electronic Configuration of Xe (before bonding)

$= 5s^2\ 5p_x^{\ 1}\ 5p_y^{\ 1}\ 5p_z^{\ 1}\ 5d_{xy}^{\ 1}\ 5d_{yz}^{\ 1}$

- Now before bonding $5s$, $5p_x$, $5p_y$, $5p_z$, $5d_{xy}$ and $5d_{yz}$ orbitals hybridize to produce six sp^3d^2 orbitals of same energy and same shape, out of which one orbital has two electrons and 5 orbitals are singly occupied which overlap with p orbitals of incoming oxygen and fluorine atoms to form five sigma bonds.

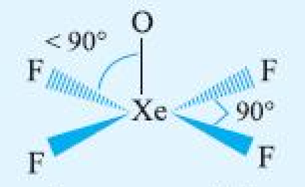
- Number of σ-bonds (bond pairs) at Xe atom = 5

  Number of lone pair of electrons at Xe atom = 1

  Total number of electron pairs

  = 5 + 1 = 6

Thus hybridisation of Xenon in $XeOF_4$ is sp^3d^2 and geometry is octaheral, however its actual shape is square pyramidal as one of the electron pairs is a lone pair.

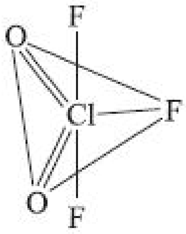


Square pyramidal
[Octahedral]

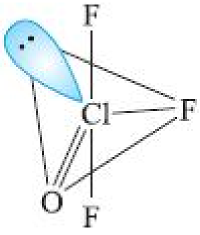
Illustration - 5 *Match the column.*

	Column 1		Column 2
(A)	ClO_2F_3	**(P)**	*Central atom is sp^3d hybridised.*
(B)	$ClOF_3$	**(Q)**	*All fluorine atoms lie in the same plane*
(C)	XeO_2F_2	**(R)**	*All fluorine atoms does not lie in same plane*
(D)	XeO_3F_2	**(S)**	*All oxygen atoms lie in equatorial plane.*
		(T)	*All lone pair of central atom lie in equatorial plane.*

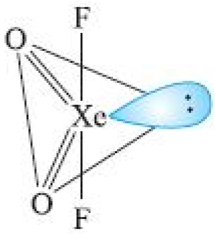
SOLUTION:



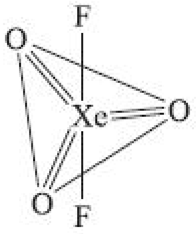
(A) : PQS



(B) : PRST



(C) : PRST

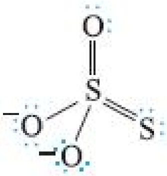


(D) : PQS

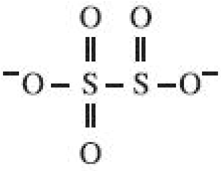
Structures of Mulitcentre Polyatomic Species :

Remember : For oxy-anions, negative charge is carried by oxygen.

1. $S_2O_3^{2-}$;

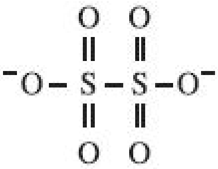


2. $S_2O_5^{2-}$;



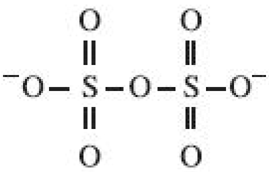
$$^{-}O-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-\overset{\overset{O}{\|}}{S}-O^{-}$$

3. $S_2O_6^{2-}$;



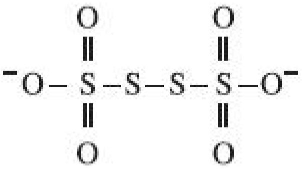
$$^{-}O-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-O^{-}$$

4. $S_2O_7^{2-}$;



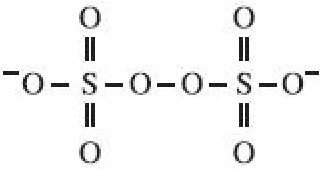
$$^{-}O-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-O-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-O^{-}$$

5. $S_4O_6^{2-}$;



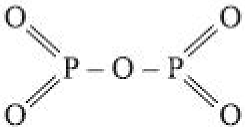
$${}^{-}O-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-S-S-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-O^{-}$$

6. $S_2O_8^{2-}$;

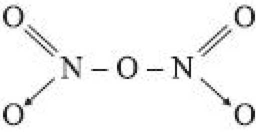


$${}^{-}O-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-O-O-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-O^{-}$$

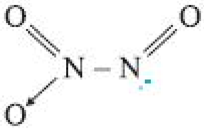
7. P_2O_5 ;



8. N_2O_5 ;

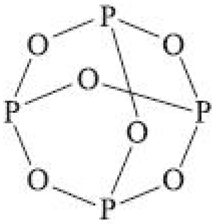


9. N_2O_3 ;

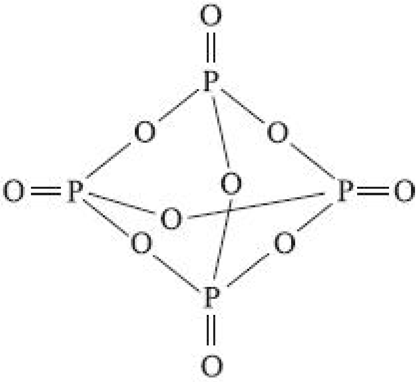


10. N_2O ; $\overset{\ominus}{N}=\overset{\oplus}{N}=O$

11. P_4O_6 ;



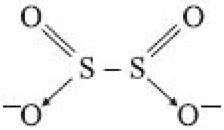
12. P_4O_{10} ;



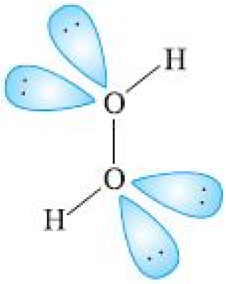
13. N_2O_4 ;

14. NO_2 ;

15. $S_2O_4^{2-}$;



16. H_2O_2 ;

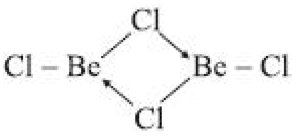


Open book type structure

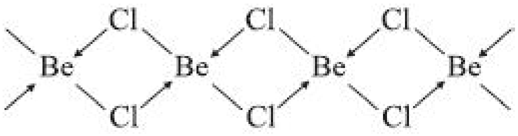
17. Berylium Chloride

(a) In vapour state (at very high temperature T > 1200 K) Cl-Be-Cl

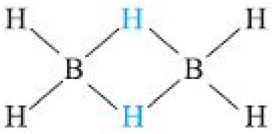
(b) In vapour state (at lower temperature T < 1200 K)



(c) In solid state

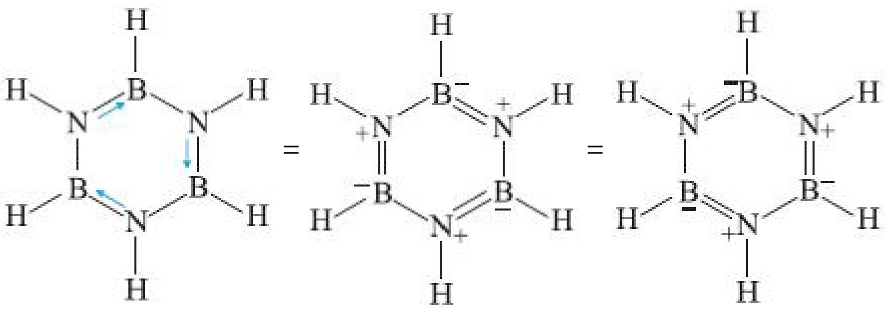


18. Diborane

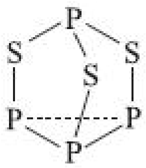


Note : Diborane is a dimer of borane BH3 and it shows 3c-2e bond (banana bond) a multicentre bond.

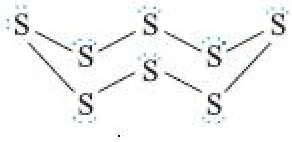
19. Inorganic Benzene:



20. P_4S_3 :



21. Sulphur (S_8) :



22. Carbon suboxide (C_3O_2) : O=C=C=C=O

23. Hydrazoic acid(HN_3) : $H-N=\overset{+}{N}=\overline{N}$

24. Phosphorus (P_4) :

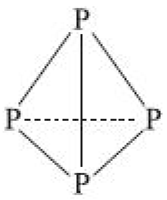


Illustration - 6 *IF_5 in liquid state can conduct electricity because it dissociate to form cation and anion according to the following reaction, $2IF_5 \rightarrow IF_4^+ + IF_6^-$. Draw the structure and determine hybridisation of all the species.*

SOLUTION :

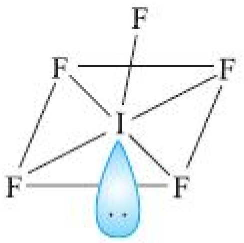
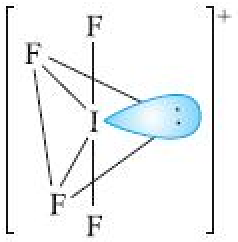
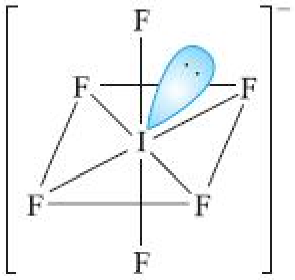
Species	**N/ 2 Value**	**No. of $l-p$**	**Shape**	**Structure**
IF_5	$\frac{12}{2}=6$	1	Sq. pyramidal	
IF_4^+	$\frac{10}{2}=5$	1	See-saw shaped	
IF6-	$\frac{14}{2}=7$	1	Capped octahedron	

Illustration - 7 *I_2Cl_6 is a yellow solid. In liquid state, it dissociated to form ions, the cation has sp^3 hybridisation and anion has sp^3d^2 hybridization and anion has sp^3d^2 hybridization. Find the exact structure of cation and anion, if 1 molecule of I_2Cl_6 dissociate to form 1 cation and 1 anion having unit charge each.*

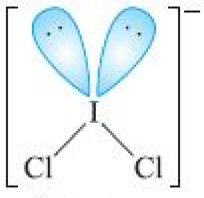
SOLUTION :

$$I_2Cl_6 \rightarrow ICl_n^+ + ICl_{6-n}^-$$

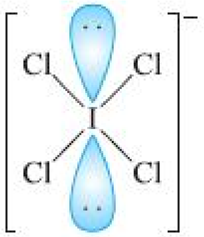
$$ICl_n^+ : \ \frac{N}{2} = 4 = \frac{7+n-1}{2} = \frac{6+n}{2}$$

$8 = 6 + n, n = 2$

∴ Cation is ICl_2^+ and anion is ICl_4^-.



sp^3 hybridization
bent shaped



sp^3d^2 hybridization
bent shaped

Illustration - 8 *PCl_5 is covalent in gaseous state but ionic in liquid and solid state. Find the actual structure of covalent PCl_5, cationic form and anionic part in liquid or solid state.*

SOLUTION :

$$PCl_5 \rightarrow PCl_4^+ + PCl_6^-$$

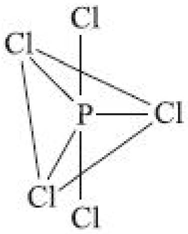
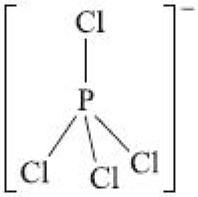
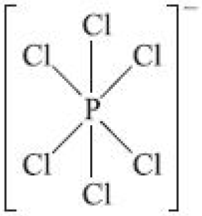
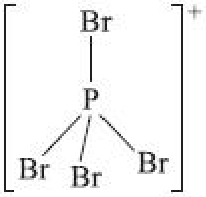
Species	N/2 Value	No. of $l-p$	Shape	Structure
PCl_5	$\frac{10}{2}=5$	0	Trigonal bipyramidal	
PCl_4^+	$\frac{8}{2}=4$	0	Tetrahedral	
PCl6-	$\frac{12}{2}=6$	0	Octahedral	

Illustration - 9 *PBr_5 exist in solid state as PBr_4^+ and Br^-. Find the hybridisation of PBr_4^+. PI_5 exist in the same manner as that of PBr_5 as PI_4^+ and I^-. Draw the structure of PI_4^+.*

SOLUTION :

$$PBr_4^+ \ : \ \frac{N}{2}=\frac{5+4-1}{2}=\frac{8}{2}=4$$

sp3 hybridization, tetrahedral shape.



$$PI_4^+ \ : \ \frac{N}{2}=\frac{5+4-1}{2}=\frac{8}{2}=4$$

sp3 hybridisation, tetrahedral shape.

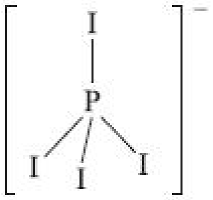
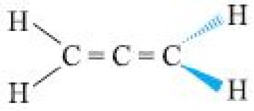
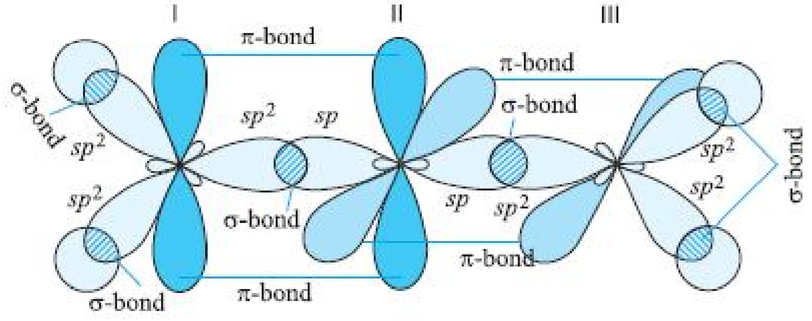


Illustration - 10 *Discuss the hybridization of carbon atoms in allene (C_3H_4) and show the p-orbital overlaps.*

SOLUTION :



Non-planar



Allene is $\overset{\text{I}}{CH_2}=\overset{\text{II}}{C}=\overset{\text{III}}{C}H_2$ carbon atoms I and III are in sp^2 hybridized state while carbon II is in sp hybridized state. Two unhybridized orbitals of carbon II overlap sidewise to form π-bonds besides it also forms a sigma bond with each of the carbon atoms using hybridized orbitals. Two hybridized orbitals of each of carbon I and III form sigma bonds with hydrogen atoms.

Effect of Electronegativity

NF_3 and NH_3 both have structures based on tetrahedron with one corner occupied by a lone pair. The high electronegativity of F pulls the bonding electronics further away from N than in NH_3. Thus, repulsion between bond pairs is less in NF_3 than NH_3. Hence, the lone pair in NF_3 causes a greater distortion from tetrahedral and gives F – N – F bond angles of $102^\circ\ 30'$ compared with $107^\circ 48'$ in NH_3. The same effect is found in H_2O (bond angle $104^\circ\ 27'$) and F_2O (bond angle 102°) and also in H_2O (bond angle 104° 27’) and H_2S (bond angle 90°).

Isoelectronic Principle

Isoelectronic species usually have the same structure. This may be extended to species with the same number of valence electrons (on the central atom).

Species	Structures
CH_4, NH_4^+, BF_4^-	Tetrahedral
CO_3^{2-} , NO_3^- , SO_3	Planar Triangle
CO_2 , N_3^- , NO_2^+	Linear

Illustration - 11 *One member of each of the following sets of compounds is not iso-electronic with the others. Which one in each set is the odd one out?*

(a) NO_2^-, CO_2 NO_2^+ and N_3^- **(b)** CN^-, N_2, CO, NO^+ and O_2^{2-}

(c) SiF_6^{2-}, PF_6^-, AlF_6^{3-} and BrF_6^-

SOLUTION :

(a) NO_2^+, CO *and* N_3^- are isoelectronic and have same structure that is linear while NO_2^- is angular

(b) CN^-, N_2, CO *and* NO^+ are isoelectronic, all have 14 electrons.

(c) SiF_6^{2-}, PF_6^-, AlF_6^{3-} are iso-electronic and have octahedral geometry. BrF_6^- has pentagonal bipyramidal geometry.

Illustration - 12 *According to valence bond theory which one of the following isoelectronic species shows resonance.*

$$N_2, CO, [CN]^-, [NO]^+$$

SOLUTION :

CO, $[CN]^-$ and $[NO]^+$ shows resonance and N_2 does not show resonance.

MOLECULAR ORBITAL THEORY Section - 4

Molecular Orbital Theory for the Formation of Covalent Bond

1. This theory suggest that when two atoms come close towards each other, then the atomic orbitals of each atom overlaps with each other to form new bigger orbitals known as Molecular Orbitals (MO).

2. When atomic orbitals overlap then two MOs are produced.

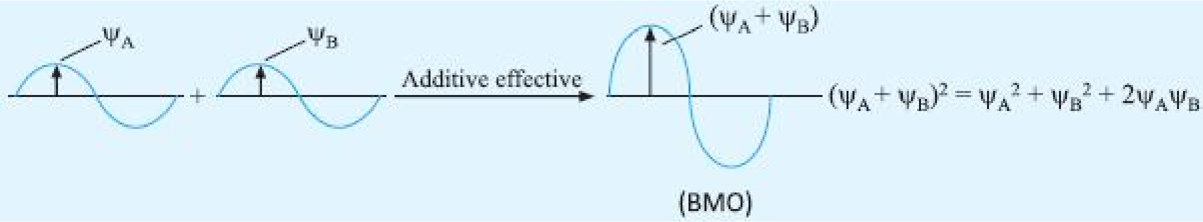
(a) Bonding Molecular Orbital (BMO)

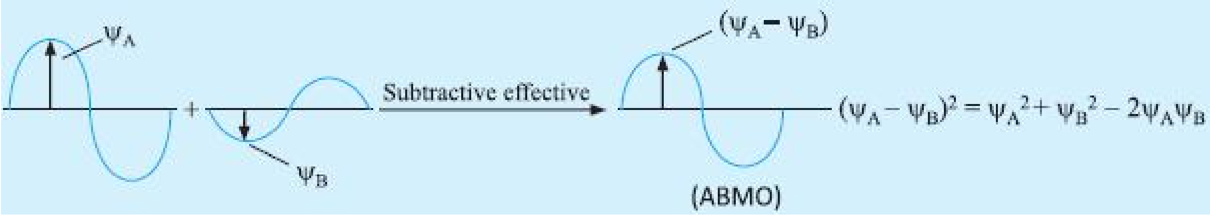
(b) Anti-bonding Molecular Orbital (ABMO)

3. Bonding molecular orbital has less energy than separate atomic orbital.
4. Anti-bonding molecular orbital has higher energy than separate atomic orbital.
5. These new MOs are spread over the atomic nuclei of both the atoms, consequently, the electrons present in the MOs are attracted by both the nuclei.

Linear Combination of Atomic Orbitals (LCAO)

According to the principle of Linear Combination of Atomic Orbitals (LCAO), bonding MO is formed by addition of wave functions (constructive interference) of the electron waves of atomic orbitals while anti-bonding MO is formed by substraction of the wave functions of the atomic orbitals (destructive interference).

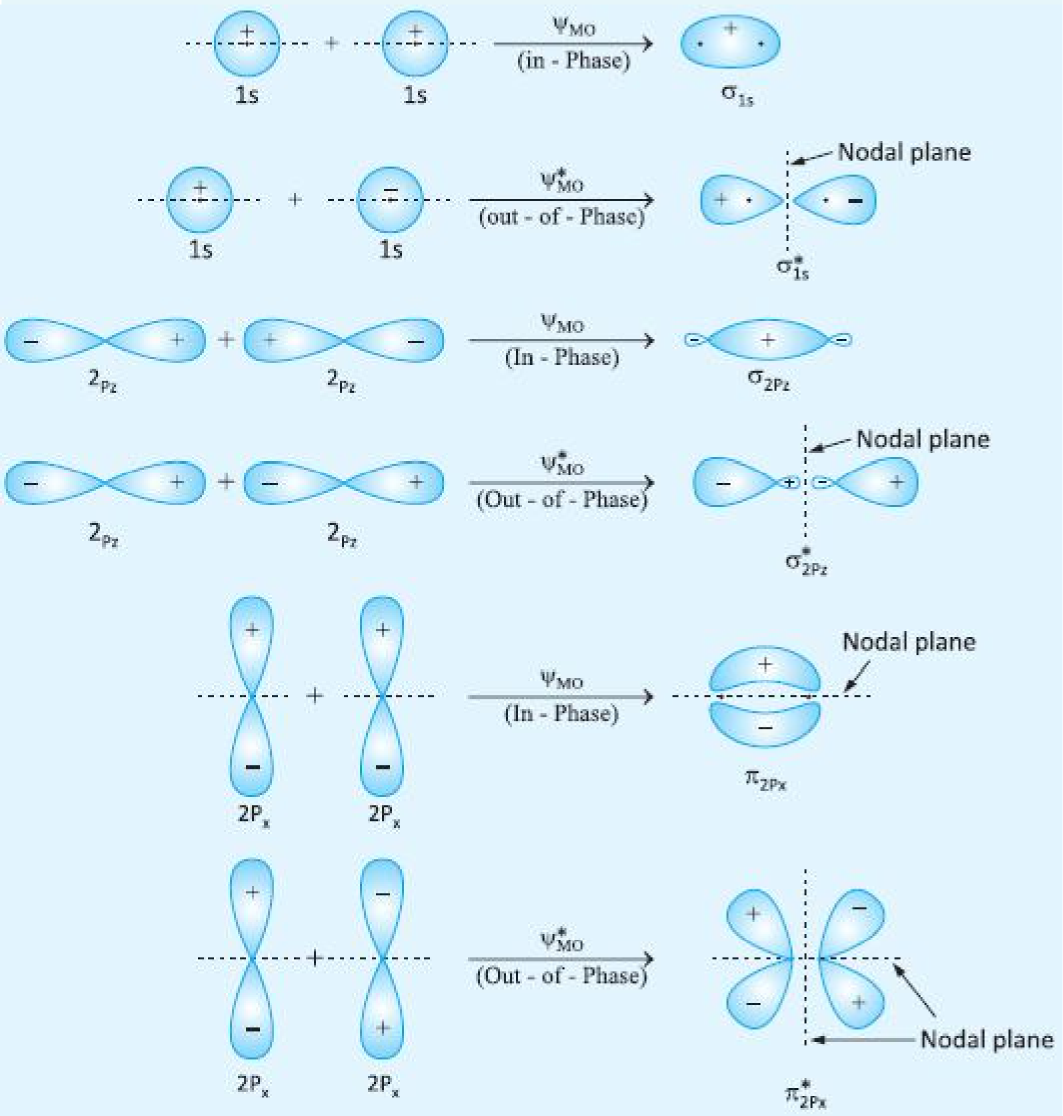




Note : Ψ_{MO} is an in-phase (bonding) interaction whereas Ψ^*_{MO} is an out of phase (anti-bonding) interaction. Further out of phase interaction results in a nodal plane in the MOs.

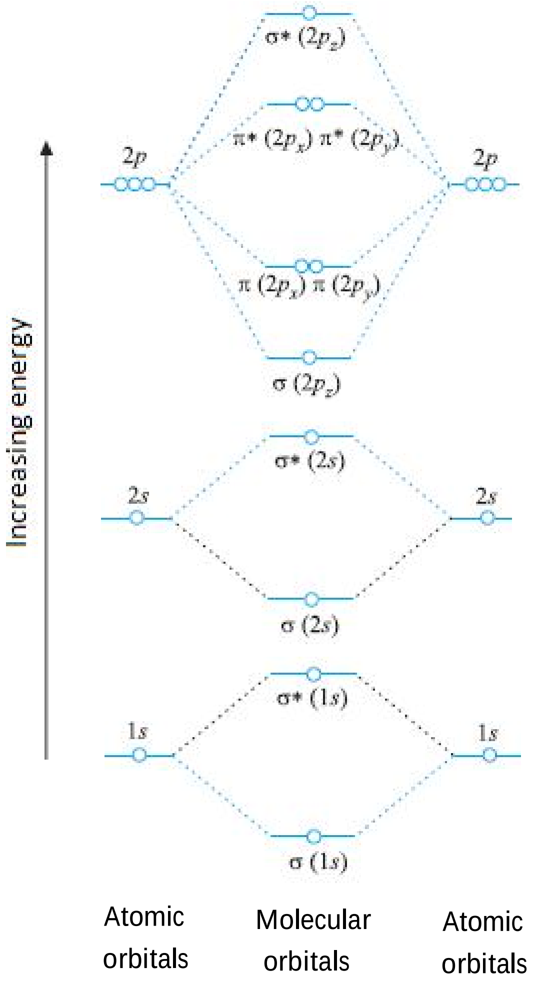
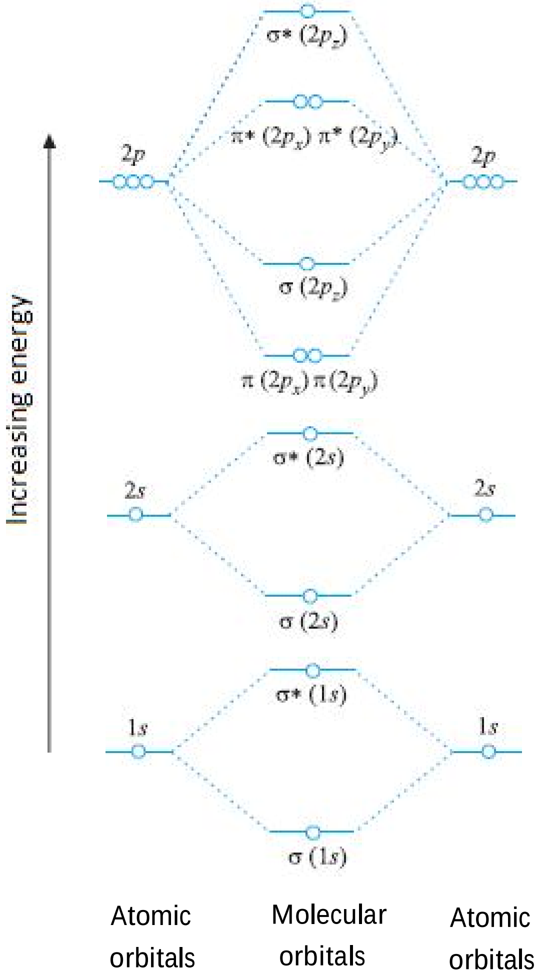
1. Only AO's of comparable energies and proper orientations combine to form MO's. For example, 1*s* can combine with 1s and not with 2*s*. Similarly, if *z* is the molecular axis p_z can combine with p_z but not with p_x or p_y to form σ-molecular orbitals.
2. The bonding MO's are represented as σ and π while the corresponding anti-bonding MO's are represented as σ^*, and π^*. Of the 2*p* orbitals, if *z* is the molecular axis, two p_z orbitals form σ bond, i.e. $\sigma(2p_z)$ while $2p_x$ and $2p_y$ orbitals form π - bonds, i.e., $\pi\ (2p_x)$, $\pi\ (2p_y)$, $\pi^*\ (2p_x)$ and $\pi^*\ (2p_y)$.
3. The shapes of MO's formed depend upon the type of the combining AO's.

Atomic Orbital Interaction diagrams :



4. The filling of the MO's occurs according to the same principle as applicable to filling of AO's i.e., Aufbau principle (MO's are filled in order of their increasing energies), Pauli's exclusion principle (a MO can have a maximum of two electrons and these must have opposite spins) and Hund's rule of maximum multiplicity (pairing of electrons in degenerate MO's does not take place until each one of the them has one electron with the same spin).

5. Molecular Orbital Diagram :

For atoms with atomic number greater than 7 e.g., O_2, F_2 or For species with total number of electrons greater than 14 e.g., NO	For atoms with atomic number less than or equal to 7 e.g., H_2, C_2, N_2 or For species with total number of electrons less than 14 e.g., B_2 C_2, CN^-
	

Note : The ordering of the MOs in B2, C2 and N2 is different from that in F2 and O2 because of orbital mixing.

6. Magnetic Character :

If all the electrons in a molecule are paired, the compound is diamagnetic; while when the molecule has one or more electrons unpaired, it will be paramagnetic.

7. The stability of the molecule formed or the strength of bonds between the bonding atoms is determined by bond order.

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

N_b : Number of electrons in bonding molecular orbitals.

N_a : Number of electrons in anti-bonding molecular orbitas.

- Greater the bond order, greater is the stability of the molecule.
- A bond order of +1 indicates that the specie is stable and that the two atoms in a molecule are held together by a single bond. A bond order of +2 indicates that the specie is stable and that the two atoms are united together with a double bond. A bond order of +3 indicates that the specie is stable and that the two atoms are held together by a triple bond.
- Bond order may be fractional and even zero.
- A zero bond order indicates the equal number of bonding and anti-bonding electrons.
- When bond order is less than zero, the species does not exist.
- A bond order of + 1/2 indicates that the species exists but is unstable, e.g. H_2^+ and He_2^+.
- The bond order of a molecule is directly proportional to its bond dissociation energy and inversely proportional to its bond length. For example,

Molecule	Bond order	Bond length	Bond diss. Energy (kJ mol^{-1})
Li_2 (Li—Li)	1	267 pm	110
B_2 (B—B)	1	159 pm	297
F_2 (F—F)	1	142 pm	158
C_2 (C = C)	2	124 pm	607
O_2 (O = O)	2	121 pm	498
N_2 (N ≡ N)	3	110 pm	945
CO ($\overset{-}{C} = \overset{+}{O}$)	3	113 pm	1076

Note : We cannot exactly correlate particular values of the bond dissociation enthalpy and distance with a given bond order. Factors such as inter-nuclear and inter-electron repulsion play an important part in determining the observed values of these parameters.

Structures of some Homonuclear Diatomic Molecules

(i) Hydrogen molecule (H_2) :

Total number of electrons in 2H atoms = 1 + 1 = 2

Electronic configuration of H_2 molecule = $\sigma 1s^2$

$$\text{Bond order} = \frac{1}{2}\left(N_b - N_a\right) = \frac{1}{2}\left(2-0\right) = 1$$

(ii) Hydrogen molecule ion, H_2^+ :

Number of electrons in $H_2^+ = 2 - 1 = 1$

Electronic configuration = $\sigma 1s^1$

$$\therefore \quad \text{Bond order} \quad \frac{1}{2}\left(1-0\right) = \frac{1}{2}$$

Since the bond order is $\frac{1}{2}$, H_2^+ ion can exist but it is unstable. Further as it has 1 unpaired electron,it is paramagnetic.

(iii) **B_2 :** B_2 is found only in the gas phase ; solid boron is found in several very hard forms with complex bonding, primarily involving B_{12} icosahedra [Structure of B_{12} icosahedron is described in chapter p-Block Elements - I.

B_2 is paramagnetic. The Lewis dot model cannot account for the paramagnetic behaviour of this molecule. The electronic configuration of boron atom shows that it has 5 electrons, hence the molecular orbitals of B_2 molecule have 10 electrons which are distributed in the following manner.

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

Note : K indicates first bonding MO and K* antibonding MO, thus KK* is same as $\sigma 1s^2\ \sigma^* 1s^2$.

Thus molecular orbital of B_2 has 6 electrons in bonding and 4 electrons in anti-bonding molecular orbitals. Thus the bond order of B_2 molecule is calculated as below:

$$\text{Bond order} = \frac{1}{2}[\text{Number of bonding electrons}] - [\text{ Number of anti-bonding electrons}]$$

$$= \frac{1}{2}[6-4] = \frac{1}{2} \times 2 = 1$$

The highest energy occupied molecular orbital (HOMOs) of B2 is $\pi_{2\,P\,x}$ and $\pi_{2\,Py}$.

Note : B_2 is a good example of the energy level shift cause by the mixing of s and p orbitals. In the absence of mixing the $\sigma_{2\,Pz}$ orbital is expected to be lower in energy than the π_{2Px} and π_{2Py} orbitals and the resulting molecule would be diamagnetic. However, mixing of orbitals lowers the energy of the σ_{2s} orbital and increases the energy of the $\sigma_{2\,Pz}$ orbitals to a higher level than the $\pi_{2\,Px}$ and $\pi_{2\,Py}$ orbitals, giving the order of energies shown in molecular orbital diagram. The lowest energy unoccupied molecular orbital (LUMOs) of B_2 molecule is $\sigma_{2\,Pz}$.

(iv) **C_2 :** C_2 is found only in the gas phase. It is not a commonly encountered chemical species (carbon is more stable as diamond, graphite and the fullerenes described in chapter p-block-I).

The electronic configuration of carbon atom shows that it has 6 electrons, hence the molecular orbitals, hence the molecular orbitals of C_2 molecule have 12 electrons which are distributed in the following manner.

$$KK^*, (\sigma 2s)^2, (\sigma^* 2s)^2, (\pi 2P_x)^2\,(\pi 2P_y)^2$$

Thus molecular orbitals of C_2 has 8 electrons in bonding and 4 electrons in anti-bonding molecular orbitals. The bond order of C_2 molecule is calculated as below:

$$\text{Bond order} = \frac{1}{2}\,[\text{Number of bonding electrons}]\text{-}[\text{Number of anti-bonding electrons}]$$

$$= \frac{1}{2}\,[8 - 4] = \frac{1}{2} \times 4 = 2$$

The simple MO picture of C_2 predicts a double bonded molecule with all electrons paired, but with both highest occupied molecular orbitals (HOMOs) having π symmetry. It is unusual because it has two π bonds and no σ-bond.

Note : The acetylide ion, C_2^{2-}, is well known, particularly in compounds with alkali metals (Na_2C_2), alkaline earth metal (CaC_2), and lanthanides. According to the molecular orbitals model C_2^{2-} should have a bond order of 3. This is supported by the similar C-C distances in acetylene (C_2H_2) and calcium carbide (CaC_2).

	C-C bond distance (pm)
$HC \equiv CH$	120.5
$Ca^{2+}\,\overline{C} = \overline{C}$	119.1

(v) Nitrogen (N_2) :

The electronic configuration of nitrogen atom shows that it has 7 electrons, hence the molecular orbitals of nitrogen molecule have 14 electrons which are distributed in the following manner :

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

Thus the molecular orbital of nitrogen has 10 bonding and 4 electrons in anti-bonding orbitals. Thus the bond order or the number of bonds in nitrogen molecule may be calculated as below :

$$\text{Bond order} = \frac{1}{2}\text{ [Number of bonding electron – Number of anti-bonding electrons]}$$

$$= \frac{1}{2}[10-4] = \frac{1}{2} \times 6 = 3$$

(vi) Oxygen (O_2) :

Oxygen (Z = 8) has the electronic configuration $1s^2 2s^2 2p^4$, so 12 electrons are to be filled in the molecular orbitals of oxygen (leaving aside the electrons of the K shell). These 12 electrons are filled in the following manner :

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

Note that the 11th and 12th electrons in the molecular orbital of oxygen go to $\pi^* 2p_x$ and $\pi^* 2p_y$ orbital (Hund's rule) ; it is because of the fact that these two anti-bonding orbitals are of equal energy. Since now there are two unpaired electrons, the oxygen molecule is paramagnetic.

$$\text{Bond order} = \frac{1}{2}\text{ [Number of bonding electron – Number of anti-bonding electrons]}$$

$$= \frac{1}{2}[10-6] = 2$$

Hence, the two oxygen atoms in oxygen molecule are linked by a double bond.

(v) Molecular orbital configuration of O_2^+ :

Number of electrons in $O_2^+ = 16 - 1 = 15$

MO configuration : $KK^*, (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2 (\pi 2p_x)^2 (\pi 2p_y)^2 (\pi^* 2p_x)^1 (\pi^* 2p_y)^0$

$$\text{Bond order} = \frac{1}{2}[10-5] = 2\frac{1}{2}$$

Bond order of $+2\frac{1}{2}$ indicates that O_2^+ is more stable than O_2. As O_2^+ has 1 unpaired electrons, it is paramagnetic.

Note : The addition of one or more electrons corresponds to reduction and the removal of one or more electrons is oxidation. The addition of electrons will follow the aufbau principle ; the removal of electrons follows the same rules but in reverse.

MO Electronic Configuration of Diatomic Species having upto 14 electrons :

Molecule or ion	Total No. of Electron	Electronic Configuration							N_B	N_A	Bond order	Paramagnetic(P) Diamagnetic (D)
		$\sigma 1s$	σ^*1s	$\sigma 2s$	σ^*2s	$\pi 2p_x$	$\pi 2p_y$	$\sigma 2p_z$				
H_2	2	2							2	0	1.0	D
H_2^+	1	1							1	0	0.5	P
He_2	4	2	2						2	2	0.0	D
He_2^+	3	2	1						2	1	0.5	P
Li_2	6	2	2	2					4	2	1.0	D
Be_2	8	2	2	2	2				4	4	0.0	D
B_2	10	2	2	2	2	1	1		6	4	1.0	P
C_2	12	2	2	2	2	2	2		8	4	2.0	D
N_2	14	2	2	2	2	2	2	2	10	4	3.0	D
O_2^{2+}	14			same as N_2					10	4	3.0	D
N_2^+	13	2	2	2	2	2	2	1	9	4	2.5	P
CN^-	14			same as N_2					10	4	3.0	D

MO Electrionic Configuration of Diatomic Species having more than 14 electrons :

Molecule of ion	Total No. of Electrons	Electronic Configuration										N_B	N_A	Bond order	Paramagnetic(P) Diamagnetic (D)
		$\sigma1s$	σ^*1s	$\sigma2s$	σ^*2s	$\sigma2p_z$	$\pi2p_x$	$\pi2p_y$	π^*2p_x	π^*2p_y	σ^*2p_z				
O_2	16	2	2	2	2	2	2	2	1	1		10	6	2.0	P
O_2^+	15	2	2	2	2	2	2	2	1			10	5	2.5	P
NO	15	2	2	2	2	2	2	2	1			10	5	2.5	P
O_2^-	17	2	2	2	2	2	2	2	2	1		10	7	1.5	P
O_2^{2-}	18	2	2	2	2	2	2	2	2	2		10	8	1.0	D
F_2	18	2	2	2	2	2	2	2	2	2		10	8	1.0	D
Ne_2	20	2	2	2	2	2	2	2	2	2	2	10	10	0.0	D

Note : O_2^- superoxide ion , O_2^{2-} : peroxide ion [Rmember as a fact : Bond order of CO^+ is 3.5]

Illustration - 13 *Which of the two peroxide ion or superoxide ion has larger bond length ?*

SOLUTION :

The bond length in a molecule is dependent on bond order. The higher is the bond order, smaller will be the bond length.

Peroxide ion, O_2^{2-}

O_2^{2-}: $KK^*(\sigma\, 2s)^2\,(\sigma^*\, 2s)^2\,(\sigma\, 2p_z)^2$ $(\pi\, 2p_x)^2\,(\pi 2p_y)^2\;(\pi^*\, 2p_x)^2\;(\pi^*\, 2p_y)^2$

$$\text{Bond order} = \frac{10-8}{2} = 1$$

Superoxide ion, O_2^-

O_2^-: $KK^*(\sigma\, 2s)^2\,(\sigma\, ^*2s)^2\,(\sigma\, 2p_z)^2\,(\pi\, 2p_x)^2$ $(\pi\, 2p_y)^2\,(\pi\, ^*2p_x)^2\,(\pi\, ^*2p_y)^1$

$$\text{Bond order} = \frac{10-7}{2} = 1.5$$

Bond order of superoxide ion is higher than peroxide ion, hence bond length of peroxide ion is larger.

Illustration - 14 **(a)** *How bond energy varies form N_2^- to N_2^+ and why ?*

(b) *On the basis of molecular orbital theory what is similarity between*

(i) *F_2 and O_2^{2-}* **(ii)** *CO, N_2, NO^+ ?*

SOLUTION :

(a) Bond energy of N_2^+ = Bond energy of N_2^- because bond order is same in both the species. [However, N_2^+ is slightly more stable than N_2^- as antibonding electrons number is higher in N_2^- than in N_2^+.]

(b) **(i)** Both F_2 and O_2^{2-} have same bond order same bond length and are diamagnetic.

(ii) These are isoelectronic species, possess same bond order and same bond length.

Illustration - 15 *Arrange the following compounds in the increasing order of bond length of O – O bond O_2, $O_2[AsF_6]$, KO_2* and peroxide ion. *Explain on the basis of ground state electronic configuration of dioxygen in these molecules.*

SOLUTION :

$O_2[AsF_6]$ has O_2^+ ion while KO_2 has O_2^- ion (superoxide ion) and peroxide is O^{2-}.

E.C. of O_2 = $KK^* \sigma(2s)^2 \sigma^*(2s)^2 \sigma(2p_z)^2 \pi(2p_x)^2 \pi(2p_y)^2 \pi^*(2p_x)^1 \pi^*(2p_y)^1$

E.C. of O_2^+ = $KK^* \sigma(2s)^2 \sigma^*(2s)^2 \sigma(2p_z)^2 \pi(2p_x)^2 \pi(2p_y)^2 \pi^*(2p_x)^1$

E.C. of O_2^- = $KK^* \sigma(2s)^2 \sigma^*(2s)^2 \sigma(2p_z)^2 \pi(2p_x)^2 \pi(2p_y)^2 \pi^*(2p_x)^2 \pi^*(2p_y)^1$

E.C. of O_2^{2-} = $KK^* \sigma(2s)^2 \sigma^*(2s)^2 \sigma(2p_z)^2 \pi(2p_x)^2 \pi(2p_y)^2 \pi^*(2p_x)^2 \pi^*(2p_y)^2$

B.O. of O_2 = 1/2 (10 – 6) = 2

B.O. of O_2^+ = 1/2 (10 – 5) = 2.5

B.O. of O_2^- = 1/2 (10 – 7) = 1.5

B.O. of O_2^{2-} = 1/2 (10 – 8) = 1

Higher is the B.O., smaller is the bond length. Hence, order of O – O bond length is

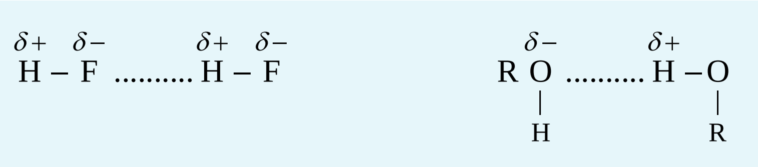
$O_2^+ > O_2 > O_2^- > O_2^{2-}$ i.e.,

$O_2[AsF_6] > O_2 > KO_2 > O_2^{2-}$

Note : bond strength $\alpha \dfrac{1}{\text{bond length}}$

CONCEPT OF HYDROGEN BONDING Section - 5

Molecules that contain F–H, O–H, N–H bonds (e.g., Water, Alcohols, Organic acids, Amines, Aromatic alcohols, etc.) show a strong tendency to associate, i.e., to link up to form larger molecules. This feature exists in solid form and as well as in solutions in certain solvents. In all of such compounds, O–H, or N–H or F–H, bond is highly polar due to large difference in electronegativity. The electrostatic attraction between such molecules should be quite strong. The positive end of one molecule attracts and is strongly attracted by the negative end of the neighbouring molecule. In this manner a large number of molecules are associated to form a cluster of molecules. Since in each case the hydrogen atom is responsible for the formation of linkages, this is known as Hydrogen bond or H–bond. It is impossible for hydrogen to form a second covalent bond so the additional linkage is shown by a dotted line. Hydrogen bonds are always of type : –A–H....B–, where A and B may be atoms of O, F, N. Hydrogen bonds are comparatively weak, with bond energies of 10–30 KJ/mol, but they are widespread and have important effect on many physical properties of many Organic and Inorganic compounds.



$$\overset{\delta+}{H} - \overset{\delta-}{F} \;\ldots\ldots\ldots\; \overset{\delta+}{H} - \overset{\delta-}{F} \qquad\qquad R\,\underset{\underset{\displaystyle H}{|}}{\overset{\delta-}{O}} \;\ldots\ldots\ldots\; \overset{\delta+}{H} - \underset{\underset{\displaystyle R}{|}}{O}$$

Types of H-Bonding :

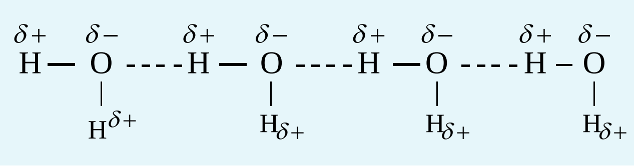
Intermolecular H-Bonding :

This type of H-bonding takes place between H and electronegative element present in the different molecules of the same substance (as in between H_2O and H_2O) or different substances (as in between H_2O and NH_3).

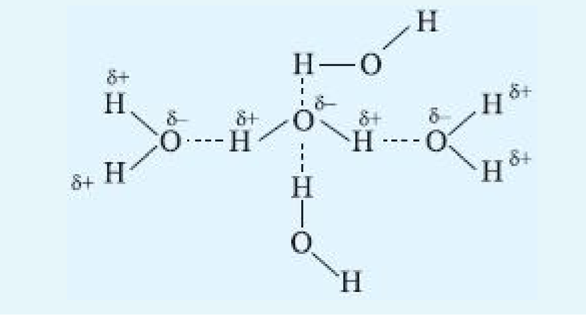
(a) In water molecules :

Due to polar nature of H_2O, there is association of water molecules giving a liquid state of abnormally high b.p.

If we actually observe, one water molecule is joined to four water molecules, two with H-atoms and other twowith O-atom. Thus coordination number of water molecules in water is four as shown in figure :



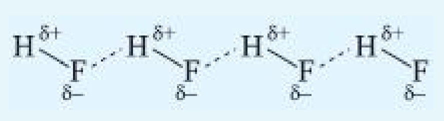
$$\overset{\delta+}{H} - \underset{\underset{\displaystyle H^{\delta+}}{|}}{\overset{\delta-}{O}} \text{----} \overset{\delta+}{H} - \underset{\underset{\displaystyle H_{\delta+}}{|}}{\overset{\delta-}{O}} \text{----} \overset{\delta+}{H} - \underset{\underset{\displaystyle H_{\delta+}}{|}}{\overset{\delta-}{O}} \text{----} \overset{\delta+}{H} - \underset{\underset{\displaystyle H_{\delta+}}{|}}{\overset{\delta-}{O}}$$



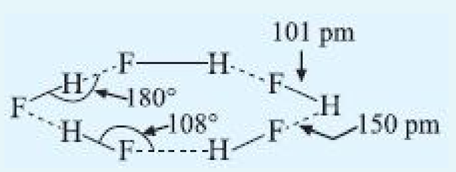
Note : Although many compounds can form intermolecular hydrogen bonds, the difference between H_2O and other polar molecules, such as NH_3 and HF, is that each oxygen atom can form two hydrogen bonds, the same as the number of lone electron pairs on the oxygen atom. Thus, water molecules are joined together in an extensive three-dimensional network in which each oxygen atom is approximately tetrahedrally boded to four hydrogen atoms, two by covalent bonds and two by hydrogen bonds. This equality in the number of hydrogen atoms and lone pairs is not characteristic of NH_3 or HF or, for that matter, of any other molecule capable of forming hydrogen bonds. Consequently, these other molecules can form rings or chains, but not three-dimensional structure.

When ice is formed from liquid water, some air gap is formed (in tetrahedral packing of water molecules). Due to this volume of ice is greater than liquid water and thus ice is lighter than water. We can say that density decreases when ice is formed. Reversely when ice melts, density increases but only upto 4°C, after this intermolecular H-bonding between water molecules breaks hence volume increases and hence density increases. Thus water has maximum density at 4°C.

(b) In hydrofluoric acid (HF), there is again association by H-bonding.

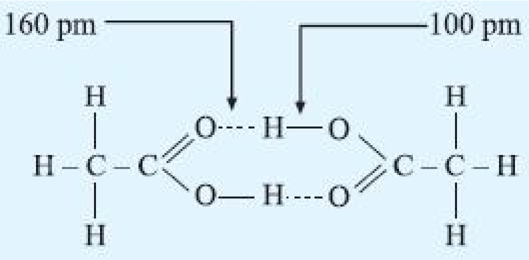


However in the gaseous state, several polymeric forms of the HF molecules exist in which the monomers are held together through H-bonding to form a pentagonal arrangement.

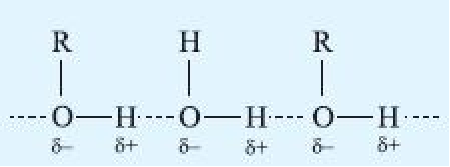


(c) There is also similar H-bonding in alcohol (R—OH) ammonia (NH_3) and phenol (C_6H_5OH) molecules.

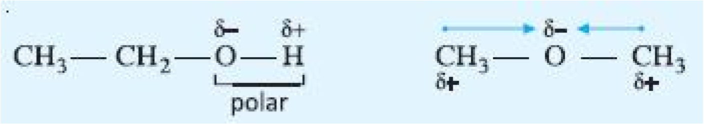
(d) Carboxylic acid dimerizes is gaseous state due to H-bonding.



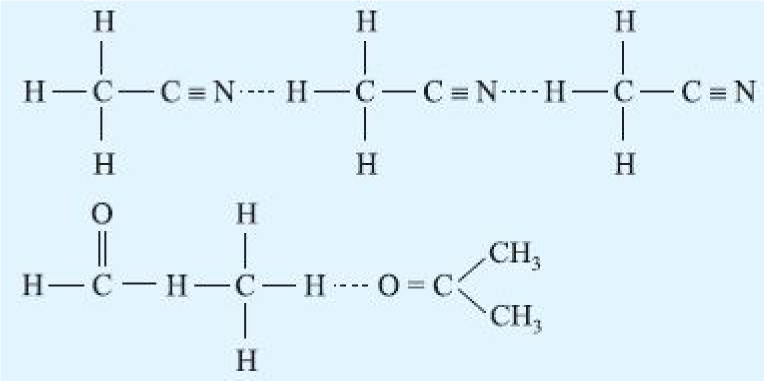
(e) Alcohol is said to be highly soluble in water due to crossed intermolecular H-bonding (between H_2O and R – OH molecules).



However isomeric ether is less soluble in water due to ether's non-polar (or weakly polar) nature.



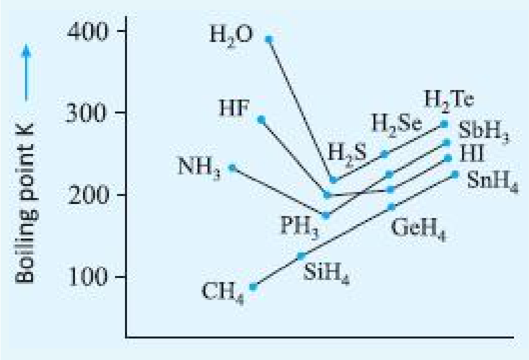
(f) Though the hydrogen atoms in a methyl groups are not polarized, if an electronegative group like chloro, carbonyl, nitro or cyano is attached to it, the C—H bond gets polarised due to the inductive effect and the hydrogen atom becomes slightly acidic resulting in the formation of weak hydrogen bonds.



Consequences of the Intermolecular Hydrogen bonding :

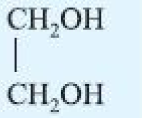
(a) Due to H-bonding boiling points of water, ammonia, hydrofluoric acid are abnormally high shown in figure.
(b) Solubility of the organic compounds in water is due to H-bond formation.

(c) Due to hydrogen-bonding, viscosity (η) of the liquid increases as given below in centipoises (CP).



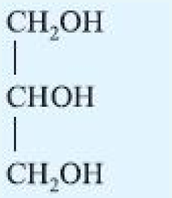
CH_3CH_2OH

η = 2 CP



CH_2OH-CH_2OH

η = 17 CP

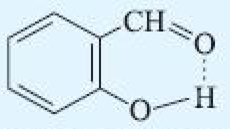


$CH_2OH-CHOH-CH_2OH$

η = 1070 CP

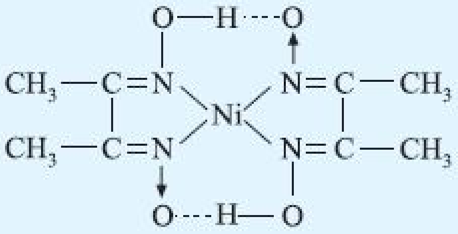
Intramolecular H-bonding :

This type of H-bonding occurs when polar H and electronegative atom are present in the same molecule.



o-hydroxy benzaldehyde

o-nitro phenol



Nickel dimethyl glyoximate (a chelate)

The necessary conditions for the formation of intramolecular hydrogen bonding are :

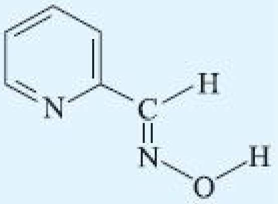
(a) The ring formed as a result of hydrogen bonding should be planar.

(b) A five or six membered ring should be formed.

(c) Interacting atoms should be placed in such a way that there is minimum strain during the ring closure.

In case of anti-form of pyridine-2-carboxaldoxime there is intramolecular hydrogen bonding but it is not shown in syn-form.

anti



syn

In this type of H–bonding, the bonding occurs within two atoms of same molecule. Such type of bonding generally occurs in aromatic organic compounds. It is also known as Chelation.

Consequences of the Intramolecular Hydrogen bonding :

Presence of Intramolecular H-bonding decreases the boiling points as well as there solubility in water.

(a) Hydrogen bonding between two atoms of the same molecule (intramolecular H-bonding) leads to unavailability of these atoms to bond with atoms of other molecule. In other words intra-molecular H-bonding between atoms of same molecule, makes them unavailable for inter-molecular H-bonding and hence compounds showing such type of bonding tends to show lower boiling points. For example, *o*-chlorophenol, o-nitrophenol and other *o*-derivatives (isomers) of hydroxy, carbonyl and acids show low boiling as well as melting points as compared to their *m*-or *p*- derivatives (which exhibit intermolecular H-bonding).

(b) The solubility of all such compounds also decreases for the same reason i.e., bonding between atoms of same molecules or chelation, does not allow these molecules to form inter-molecular bonds. For example in o-Nitrophenol, O-H group is busy making intramolecular H-bond with O atom of the NO_{2-} group and becomes unavailable for intermolecular H-bonding and hence it is very less soluble in water.

Illustration - 16 *Why H_2O is liquid while H_2S is a gas at ordinary temperature ?*

SOLUTION :

Oxygen has high electronegativity than sulphur. As a result, H_2O forms hydrogen bonding. Consequently, molecules of water come nearer to each other through hydrogen bonding. This result is higher boiling point of water and hence it is a liquid.

Illustration - 17 *The density of ice is less than that of water or ice floats over water. Explain.*

SOLUTION :

In ice, water molecule is associated with four other molecules through hydrogen bonding in a tetrahedral manner, i.e., it has open-cage like structure in which lesser molecules are paked per unit volume. When ice melts, the molecules come closer to one another. Consequently the density of water in liquid state is more than solid state. Thus, ice floats over water.

Illustration - 18 *The boiling point of H_2O is more than the boiling point of HF although fluorine is more electronegative than oxygen and form stronger H-bond.*

SOLUTION :

The strength of a hydrogen bond is determined by the coulombic interaction between the lone-pair electrons of the electronegative atom and the hydrogen nucleus. Fluorine is more electronegative than oxygen, and so we would expect a stronger hydrogen bond to exist in liquid HF *than in* H_2O. *But boiling point of* HF *is lower than that of water because each* H_2O *takes part in four intermolecular hydrogen bonds. Therefore, the forces holding the molecules together are stronger in* H_2O *than in* HF.