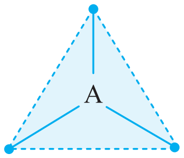
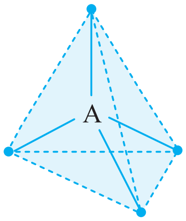
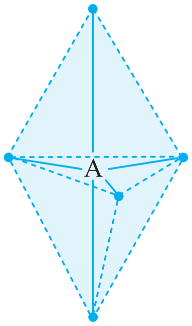
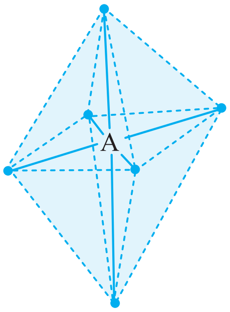
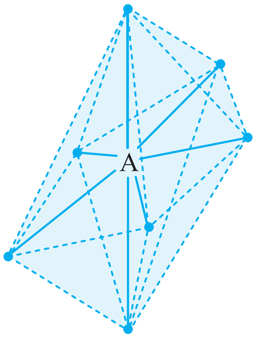
PREDICTION OF GEOMETRY (SHAPE) OF COVALENT MOLECULES Section - 2











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 $2s$ orbital to $2p$ orbital to generate two singly occupied orbitals.
- Outer Electronic Configuration of Be (after excitation of electrons) $= 2s^1\ 2p^1$.
- Now before bonding $2s$ and $2p$ 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

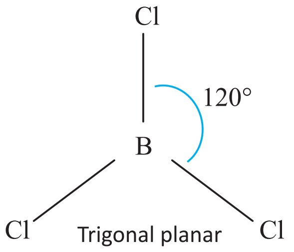
  Number of lone pair of electrons at Be atom $= 0$, Total number of electron pairs $= 2 + 0 = 2$

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

$$\text{Cl} \text{———} \text{Be} \text{———} \text{Cl}$$

Linear

(b) Boron trichloride (BCl_3)



Boron is forming three bonds with three chlorine atoms.

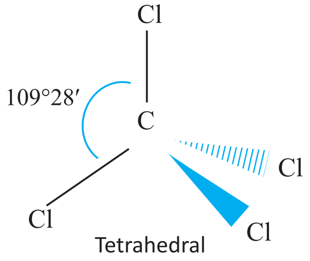
Outer Electronic Configuration of B = $2s^2\,2p^1$

- 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)



Carbon is forming four bonds with four Chlorine atoms.

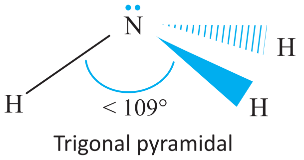
Outer Electronic Configuration of C = $2s^2\,2p^2$

- 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)



Nitrogen is forming three bonds with three hydrogen atoms.

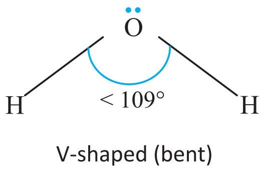
Outer Electronic Configuration of N = $2s^2\,2p^3$

- 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)



Oxygen is forming two bonds with two hydrogen atoms.

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

- Outer Electronic Configuration of O (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°.

Molecular Shapes

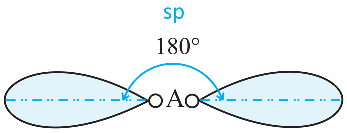
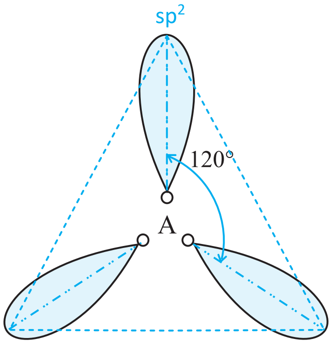
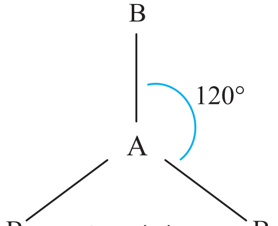
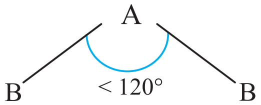
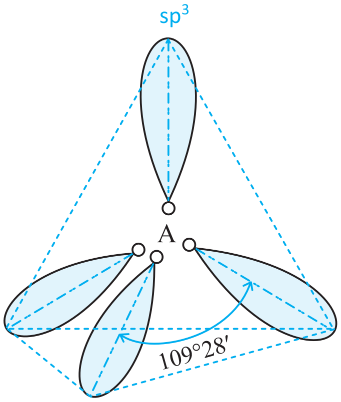
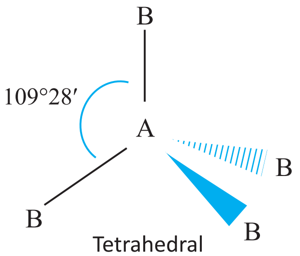
Note : **(a)** For Column 2 (Type) : Type AB_3L_2 means in this molecule central atom (denoted by A) has three bond pairs (denoted by B_3) and two lone pairs (denoted by L_2) .

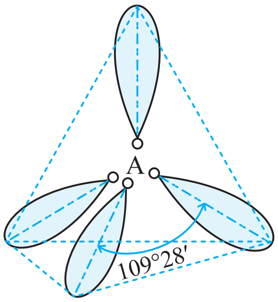
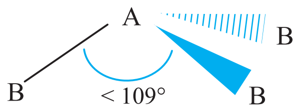
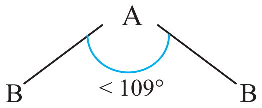
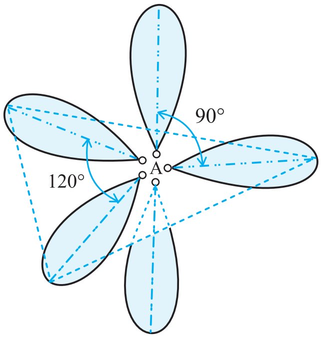
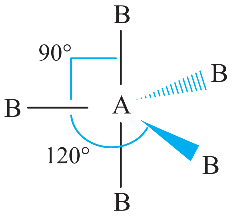
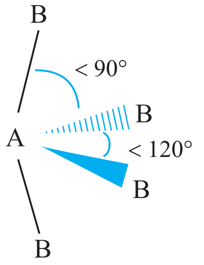
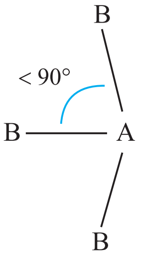
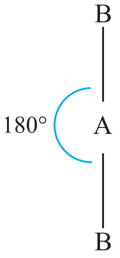
(b) For Column 3 : E = B + L

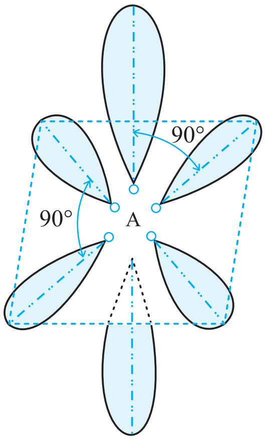
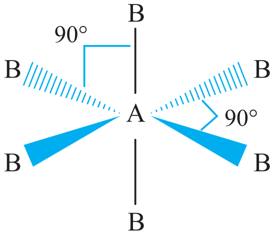
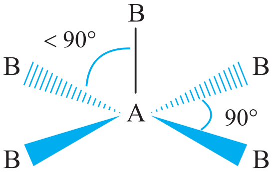
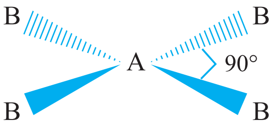
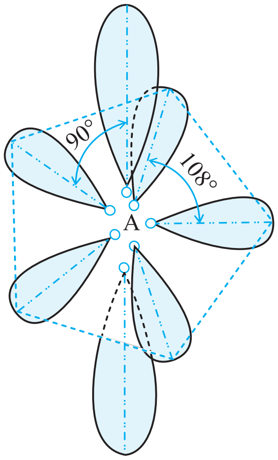
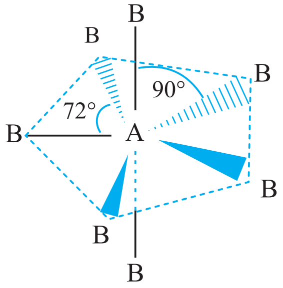
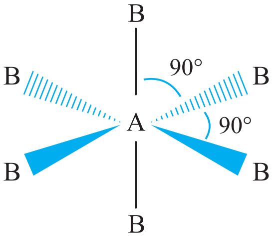
E : stands for total number of electron pairs present in the outer most shell of the central atom.

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

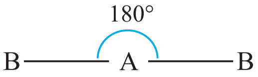
L : stands for the number of lone pairs present around the central atom.

Hybridisation and Geometry of molecules	**Type**	**E (B + L)**	**Actual shape of molecules**	**Bond Angle**	**Examples**
 Linear	AB_2	2 (2 + 0)	B ——— A ——— B Linear	180°	CO_2, $HgCl_2$, BeF_2, C_2H_2, HCN, $BeCl_2$
	ABL	2 (1 + 1)	A ——— B Linear		N_2, CN^-
 Trigonal planar	AB_3	3 (3 + 0)	 Trigonal planar	120°	BF_3, $AlCl_3$, SO_3, C_2H_4, NO_3^-, CO_3^{2-}, HCHO, C_6H_6
	AB_2L	3 (2 + 1)	 V-shape (bent)	< 120°	NO_2, SO_2, $SnCl_2$
 Tetrahedral	AB_4	4 (4 + 0)	 Tetrahedral	109°28′	CH_4, SiH_4, SO_4^{2-}, $SnCl_4$, ClO_4^-, BF_4^-, NH_4^+

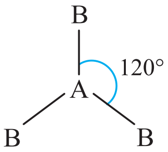
sp^3  Tetrahedral	AB_3L	4 (3 + 1)	 Trigonal pyramidal	<109.5°	NH_3, PCl_3, PH_3, AsH_3, ClO_3^-, NF_3
	AB_2L_2	4 (2 + 2)	 V-shaped (bent)	<109.5° ~ (90°-104°)	H_2O, H_2S, OF_2, NH_2^-, ClO_2^-
sp^3d  Trigonal Bipyramidal	AB_5	5 (5 + 0)	 Trigonal Bipyramidal	120° (equatorial) and 90° (Axial)	PCl_5, $SbCl_5$
	AB_4L	5 (4 + 1)	 (Bent) Seesaw, Sawhorse, folded square, (distorted/irregular) Tetrahedral	< 120° and < 90°	$TeCl_4$, SF_4, XeO_2F_2, IF_4^+
	AB_3L_2	5 (3 + 2)	 T-shaped	< 90°	ClF_3, IF_3
	AB_2L_3	5 (2 + 3)	 Linear	180°	I_3^-, XeF_2

sp^{3}d^2  Octahedral	AB_6	6 (6 + 0)	 Octahedral	90°	SF_6, PF_6^-, $SnCl_6^-$
	AB_5L	6 (5 + 1)	 Square pyramidal	90° (equatorial) and < 90° (axial)	ICl_5, BrF_5, IF_5, $XeOF_4$
	AB_4L_2	6 (4 + 2)	 Square planar	90°	XeF_4, ICl_4^-
sp^{3}d^3  Pentagonal Bipyramidal	AB_7	7 (7 + 0)	 Pentagonal bipyramidal	72° (equatorial) and 90° (axial)	IF_7
	AB_6L	7 (6 + 1)	 Distorted Octahedral	90° (equatorial) and 90° (axial)	XeF_6

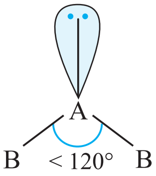
A summary of possible shapes is given on the next page.



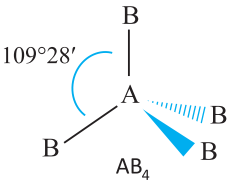
AB_2
Linear



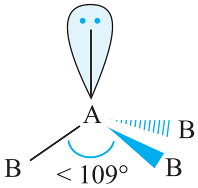
AB_3
Trigonal planar



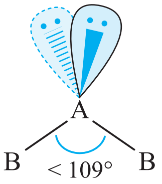
AB_2L_1
Bent or Angular



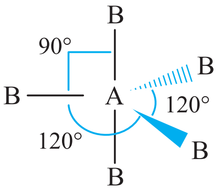
AB_4
Tetrahedral



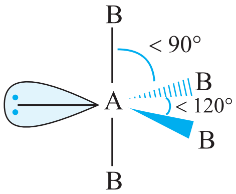
AB_3L_1
Trigonal pyramidal



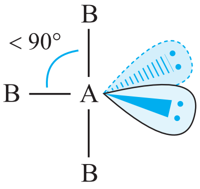
AB_2L_2
Bent or Angular



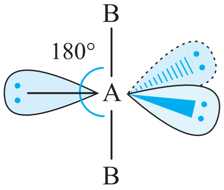
AB_4
Trigonal bipyramidal



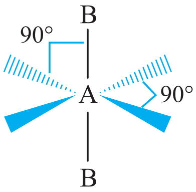
AB_4L_1
Sawhorse or Seesaw



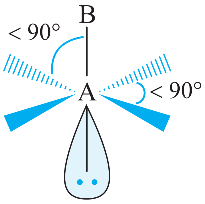
AB_3L_2
T-shape



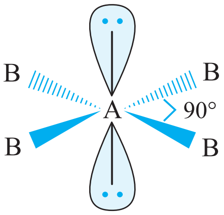
AB_2L_3
Linear



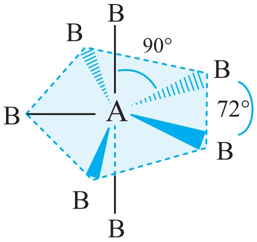
AB_6
Octahedral



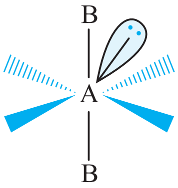
AB_5L_1
Square pyramidal



AB_4L_2
Square planar



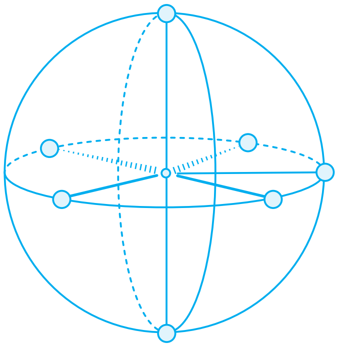
AB_7
Pentagonal bipyramidal



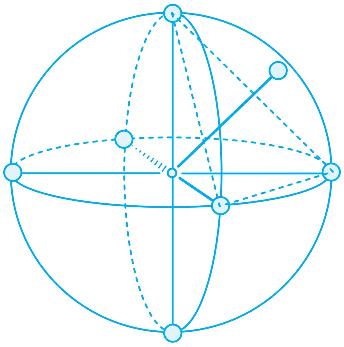
AB_6L
Distorted Octahedral

VSEPR in 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 Electronic 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 (direct) 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).

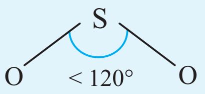
⇒ Each Oxygen will form another bond with the Sulphur atom by sideways overlap (π overlap or π bond).

⇒ 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 Electronic 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 $3s$, $3p_x$ 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 pairs is a lone 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.

$\Rightarrow$ 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).

$\Rightarrow$ Outer Electronic Configuration of S (with electrons removed) = $3s^2\ 3p_x^{\ 1}$

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

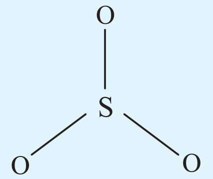
- Now before bonding $3s$, $3p_x$ and $3p_y$ orbitals hybridize to produce three sp^2 orbitals of same energy and same shape, which are singly occupied (one electron each) which overlap with p orbitals of incoming Oxygen atoms to form three sigma bonds.

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

  Number of lone pair of electrons at S atom = 0

Total number of electron pairs = 3 + 0 = 3

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



Trigonal planar

(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.

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

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

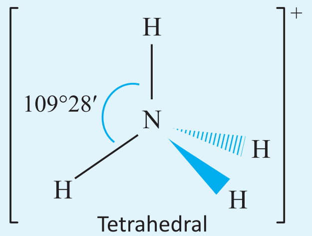
- Now before bonding $2s$, $2p_x$, $2p_y$ and $2p_z$ orbitals hybridize to produce four sp^3 orbitals of same energy and same shape, which are singly occupied (one electron each) which overlap with s orbitals of incoming hydrogen atoms to form four sigma bonds.

- 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 fluorine 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) = $5s^2\ 5p^4$

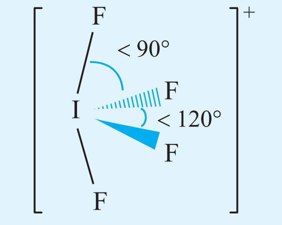
⇒ Electronic Configuration of I (after excitation of electrons) = $5s^2\ 5p_x^{\ 1}\ 5p_y^{\ 1}\ 5p_z^{\ 1}5d^1$

- Now before bonding $5s$, $5p_x$, $5p_y$, $5p_z$ and $5d$ orbitals hybridize to 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

  Total number of electron pairs = 5

Thus hybridization 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 ClF_3 molecule, chlorine forms three bonds with three fluorine atoms.

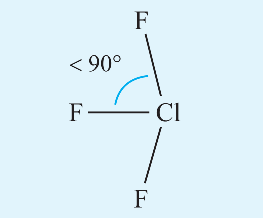
Outer Electronic Configuration of Cl = $3s^23p^5$

- Outer Electronic Configuration of Cl (before bonding) = $3s^2\ 3p_x^{\ 2}\ 3p_y^{\ 1}\ 3p_z^{\ 1}3d^1$
- Now before bonding $3s$, $3p_x$, $3p_y$, $3p_z$ and $3d$ orbitals hybridize to produce five sp^3d 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 overlap with the p orbitals of incoming fluorine atoms to form three sigma bonds.
- Number σ-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 is trigonal bipyramidal, however it actually is a T-shaped molecule because 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) = $5s^2\ 5p^6$

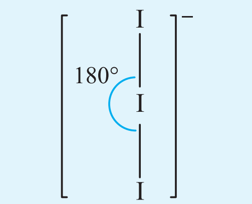
⇒ Electronic Configuration of I (after excitation of electrons) = $5s^2\ 5p_x^{\ 2}\ 5p_y^{\ 2}\ 5p_z^{\ 1}5d^1$

- Now before bonding $5s$, $5p_x$, $5p_y$, $5p_z$ and $5d$ 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.

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

$\Rightarrow$ Outer Electronic Configuration of P (after excitation of electrons)

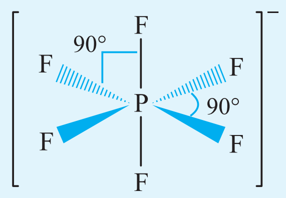
$$= 3s^1\ 3p_x{}^1\ 3p_y{}^1\ 3p_z{}^1\ 3d_{xy}{}^1\ 3d_{yz}{}^1$$

- 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 enery 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 hybridization of PF_6^- 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.

$\Rightarrow$ 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).

$\Rightarrow$ Outer Electronic Configuration of Xe (with an electron removed) = $5s^2\ 5p_x{}^2\ 5p_y{}^2\ 5p_z{}^1$

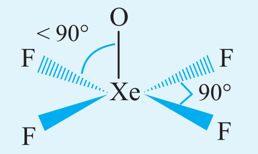
$\Rightarrow$ Outer Electronic Configuration of Xe (before bonding) = $5s^2\ 5p_x{}^1\ 5p_y{}^1\ 5p_z{}^1\ 5d_{xy}{}^1\ 5d_{yz}{}^1$

- 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 hybridization of Xenon in $XeOF_4$ is sp^3d^2 and geometry is octahedral, 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

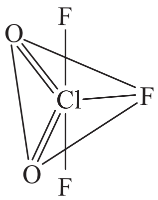
(A) ClO_2F_3
(B) $ClOF_3$
(C) XeO_2F_2
(D) XeO_3F_2

Column 2

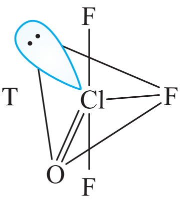
(P) *Central atom is sp^3d hybridised.*
(Q) *All fluorine atoms lie in the same plane*
(R) *All fluorine atoms does not lie in same plane*
(S) *All oxygen atoms lie in equitorial plane.*
(T) *All lone pair of central atom lie in equitorial plane.*

SOLUTION :

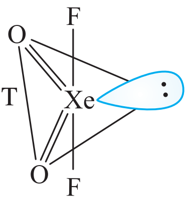
(A): PQS



(B): PQST



(C):PQST



(D):PQS

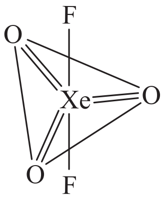


Illustration - 6 *IF_5 in liquid state can conduct electricity because it dissociate to form cation and anion according to the following reaction, $2IF_5 \longrightarrow IF_4^+ + IF_6^-$. Draw the structure and determine hybridization of all the species.*

SOLUTION :

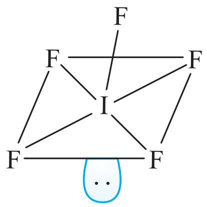
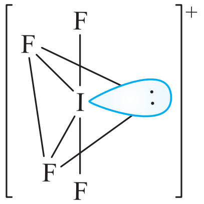
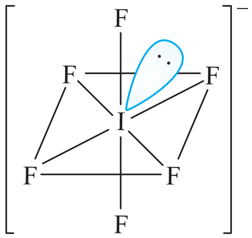
Species	**N/ 2 Value**	**No. of $l-p$**	**Shape**	**Structure**
IF_5	$\frac{12}{2} = 6$	1	Sq. pyramidal	
IF_4^+	$\frac{10}{2} = 5$	1	See-saw shaped	
IF_6^-	$\frac{14}{2} = 7$	1	Capped octahedron.	

Illustration - 7 *I_2Cl_6 is a yellow solid. In liquid state, it dissociated to form ions, the cation has sp^3 hybridization 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.*

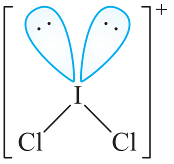
SOLUTION :

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

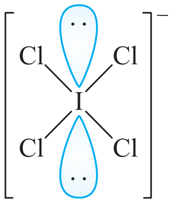
$$ICl_n^+ : \ \frac{N}{2} = 4 = \frac{7+n-1}{2} = \frac{6+n}{2}$$

$$8 = 6+n, \ n = 2$$

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



sp^3 hybridization
bent shaped



sp^3d^2 hybridization
square planar shape

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 : $PCl_5 \longrightarrow PCl_4^+ + PCl_6^-$

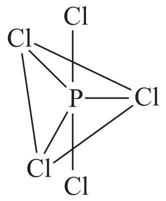
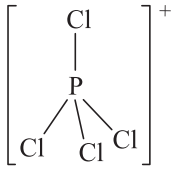
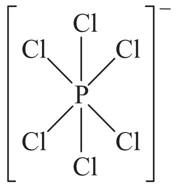
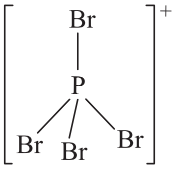
Species	**N/2 Value**	**No. of *l* – p**	**Shape**	**Structure**
PCl_5	$\frac{10}{2} = 5$	0	Trigonal bipyramidal	
PCl_4^+	$\frac{8}{2} = 4$	0	Tetrahedral	
PCl_6^-	$\frac{12}{2} = 6$	0	Octahedral	

Illustration - 9 *PBr_5 exist in solid state as PBr_4^+ and Br^-. Find the hybridization 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 :

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

sp^3 hybridization, tetrahedral shape.



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

sp^3 hybridization, tetrahedral shape.

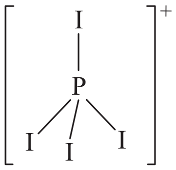
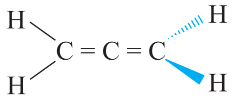


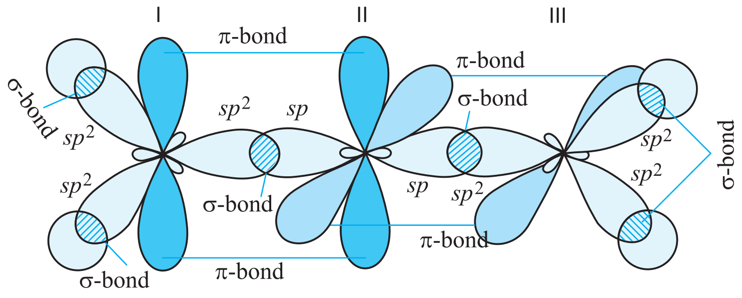
Illustration - 10 *Discuss the hybridization of carbon atoms in allene (C_3H_4) and show the p-orbital overlaps.*

SOLUTION :

Allene is $\overset{I}{CH_2} = \overset{II}{C} = \overset{III}{CH_2}$ 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. Allene is non-planar molecule.



Non-planar



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 electrons 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 $104^\circ\ 27'$) 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 folowing sets of compounds is not iso-electronic with the others. Which one in each set is the odd one out ?*

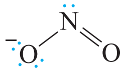
(a) $NO_2^-, CO_2\ NO_2^+$ *and* N_3^- **(b)** CN^-, N_2, CO, NO^+ *and* O_2^{2-}

(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

$:\ddot{O}=\overset{+}{N}=\ddot{O}:$ $:\ddot{O}=C=\ddot{O}:$ $:\underset{..}{\bar{N}}=\overset{+}{N}=\underset{..}{\bar{N}}:$



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

$:\bar{C}\equiv N:$ $:N\equiv N:$ $:\bar{C}\equiv\overset{+}{O}:$ $:N\equiv\overset{+}{O}:$

(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.

$:N\equiv N:$

$:C=\ddot{O}: \longleftrightarrow :\bar{C}\equiv\overset{+}{O}:$; $:\overset{+}{N}=\ddot{O}: \longleftrightarrow :N\equiv\overset{+}{O}:$; $:C=\ddot{\bar{N}}: \longleftrightarrow :\bar{C}\equiv N:$

IN-CHAPTER EXERCISE-A

Choose the correct alternative. Only One Choice is Correct. However, questions marked with * may have More than One Correct option : :

1. The compound which contains both ionic and covalent bonds is :

(A) CH_4 (B) H_2 (C) KCN (D) KCl

2. The octet rule is not valid for the molecule :

(A) CO_2 (B) H_2O (C) O_2 (D) $BeCl_2$

3. Element X is strongly electropositive and element Y is strongly electronegative. Both are univalent. The compound formed would be :

(A) X^+Y^- (B) X^-X^+

(C) $X-Y$ (D) $X \longrightarrow Y$

4. Which of the following compounds are covalent ?

(A) H_2 (B) CaO

(C) KCl (D) Na_2S

5. The total number of electrons that take part in forming the bond in N_2 is :

(A) 2 (B) 4 (C) 6 (D) 10

6. If a molecule MX_3 has zero dipole moment, the sigma bonding orbitals used by M (atomic number < 21) are :

(A) pure *p* (B) *sp* hybrid

(C) sp^2 hybrid (D) sp^3 hybrid

7. Among the following, the molecule that is linear is :

(A) CO_2 (B) NO_2

(C) SO_2 (D) ClO_2

8. The compound with no dipole moment is :

(A) methyl chloride

(B) carbon tetrachloride

(C) methylene chloride

(D) chloroform

9. Carbon tetrachloride has no net dipole moment because of :

(A) its planar structure

(B) its regular tetrahedral structure

(C) similar sizes of carbon and chlorine

(D) similar electron affinities of carbon and chlorine

10. The set representing the correct order of ionic radius is :

(A) $Li^+ > Na^+ > Mg^{2+} > Be^{2+}$

(B) $Mg^{2+} > Be^{2+} > Li^+ > Na^+$

(C) $Li^+ > Be^{2+} > Na^+ > Mg^{2+}$

(D) $Na^+ > Li^+ > Mg^{2+} > Be^{2+}$

11. On hybridization of one *s* and one *p* orbitals we get :

(A) two mutually perpendicular orbitals

(B) two orbitals at 180°

(C) four orbitals directed tetrahedrally

(D) three orbitals in a plane

12. The bond between two identical non-metal atoms has a pair of electrons :

(A) unequally shared between the two

(B) transferred fully from one atom to another

(C) with identical spins

(D) equally shared between them

13. The hybridisation of sulphur in sulphur dioxide is :

(A) *sp* (B) sp^3 (C) sp^2 (D) dsp^2

14. The species in which the central atom uses sp^2 hybrid orbitals in its bonding is :

(A) PH_3 (B) NH_3

(C) CH_3^+ (D) SbH_3

15. The molecule that has linear structure is :

(A) CO_2 (B) NO_2 (C) SO_2 (D) SiO_2

16. The molecule which has zero dipole moment is :

(A) CH_2Cl_2 (B) BF_3 (C) NF_3 (D) ClO_2

17. The molecule which has pyramidal shape is :

(A) PCl_3 (B) SO_3 (C) CO_3^{2-} (D) NO_3^-

18. The compound in which $\overset{*}{C}$ uses the sp^3 hybrid orbitals for bond formation is :

(A) $H\overset{*}{C}OOH$ (B) $(H_2N)_2\overset{*}{C}O$

(C) $(CH_3)_3\overset{*}{C}OH$ (D) $CH_3\overset{*}{C}HO$

19. The type of hybrid orbitals used by the chlorine atom in ClO_2^- is :

(A) sp^3 **(B)** sp^2
(C) sp **(D)** None of these

20. The cyanide ion, CN^- and N_2 are isoelectronic. But a contrast to CN^-, N_2 is chemically inert, because of :

(A) low bond energy
(B) absence of bond polarity
(C) unsymmetrical electron distribution
(D) presence of more number of electrons in bonding orbitals.

21. Which one is most ionic ?

(A) P_2O_5 **(B)** CrO_3
(C) MnO **(D)** Mn_2O_7

22. Number of paired electrons in O_2 molecule is :

(A) 7 **(B)** 8 **(C)** 16 **(D)** 14

23. Among the following species, identify the isostructural pairs. $NF_3, NO_3^-, BF_3, H_3O^+, HN_3$

(A) $[NF_3, NO_3^-]$ and $[BF_3, H_3O^+]$
(B) $[NF_3, HN_3^-]$ and $[NO_3^-, BF_3]$
(C) $[NF_3, H_3O^+]$ and $[NO_3^-, BF_3]$
(D) $[NF_3, H_3O^+]$ and $[HN_3, BF_3]$

24. Among the following compounds the one that is polar and has the central atom with sp^2 hybridisation is :

(A) H_2CO_3 **(B)** SiF_4
(C) BF_3 **(D)** $HClO_2$

25. Which contains both polar and non-polar bonds ?

(A) NH_4Cl **(B)** HCN
(C) H_2O_2 **(D)** CH_4

26. The critical temperature of water is higher than that of O_2 because the H_2O molecule has :

(A) fewer electrons than O_2
(B) two covalent bonds
(C) V-shape
(D) dipole moment.

27. Which one of the following compounds has sp^2 hydridization?

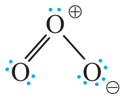
(A) CO_2 **(B)** SO_2 **(C)** N_2O **(D)** CO

For Questions 28 - 29

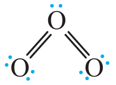
(A) Statement 1 is true, Statement 2 is true and it is correct explanation for Statement 1
(B) Statement 1 is true, Statement 2 is true but it is NOT a correct explanation for Statement 1
(C) Statement 1 is true, Statement 2 is false
(D) Statement 1 is false, Statement 2 is true

28. Statement 1 :

The electronic structure of O_3 is



Statement 2 :



structure is not allowed because octet around O cannot be expanded.

29. Statement 1 :

LiCl is predominantly covalent compound

Statement 1 :

Electronegativity difference between Li and Cl is too small.

30. The correct order of increasing C — O bond length of CO, CO_3^{2-} CO_2, is :

(A) $CO_3^{2-} < CO_2 < CO$ **(B)** $CO_2 < CO_3^{2-} < CO$
(C) $CO < CO_3^{2-} < CO_2$ **(D)** $CO < CO_2 < CO_3^{2-}$

31. The geometry of H_2S and its dipole moment are :

(A) angular and non-zero
(B) angular and zero
(C) linear and non-zero
(D) linear and zero

32. Molecular shapes of SF_4, CF_4 and XeF_4 are :

(A) the same, with 2, 0 and 1 lone pairs of electrons respectively.
(B) the same, with 1, 1 and 1 lone pairs of electrons respectively.
(C) different, with 0, 1 and 2 lone pairs of electrons respectively.
(D) different, with 1, 0 and 2 lone pairs of electrons respectively.

33. The hybridisation of atomic orbitals of nitrogen in NO_2^+, NO_3^- and NO_4^+ are :

(A) sp, sp^3 and sp^2 respectively
(B) sp, sp^2 and sp^3 respectively
(C) sp^2, sp and sp^3 respectively
(D) sp^2, sp^3 and sp respectively

34. The correct order of hybridization of the central atom in the following species NH_3, PCl_4^-, PCl_5 and BCl_3 is :
(A) dsp^2, sp^3d, sp^2 and sp^3
(B) sp^3, sp^3d, sp^3d, sp^2
(C) dsp^2, sp^2, sp^3, dsp^3
(D) dsp^2, sp^3, sp^2, dsp^3

35. Specify the coordination geometry around and hybridisation of N and B atoms in a 1 : 1 complex of BF_3 and NH_3 :
(A) N : tetrahedral, sp^3 ; B : tetrahedral, sp^3
(B) N : pyramidal, sp^3 ; B : pyramidal, sp^3
(C) N : pyramidal, sp^3 ; B : planar, sp^2
(D) N : pyramidal, sp^3 ; B : tetrahedral, sp^3

36. Identify the least stable ion amongst the following :
(A) Li^- **(B)** Be^- **(C)** B^- **(D)** C^-

37. Which of the following are isoelectronic and isostructural ? NO_3^-, CO_3^{2-}, ClO_3^-, SO_3
(A) NO_3^-, CO_3^{2-} **(B)** SO_3, NO_3^-
(C) ClO_3^-, CO_3^{2-} **(D)** CO_3^{2-}, SO_3

38. Which species has the maximum number of lone pair of electrons on the central atom ?
(A) $[ClO_3]^-$ **(B)** XeF_4
(C) N_2O **(D)** $[I_3]^-$

***39.** CO_2 is isostructural with :
(A) $HgCl_2$ **(B)** $SnCl_2$
(C) C_2H_2 **(D)** NO_2

***40.** The linear structure is assumed by :
(A) $SnCl_2$ **(B)** NCO^-
(C) CS_2 **(D)** NO_2^+

***41.** The molecules that will have dipole moment are :
(A) 2, 2-Dimethylpropane
(B) *trans*-2-Pentene
(C) *cis*-3-Hexene
(D) 2, 2, 3, 3-Tetramethylbutane

***42.** Pick out the isoelectronic structures from the following :
I. CH_3^+ II. H_3O^+
III. NH_3 IV. CH_3^-
(A) I and II **(B)** III and IV
(C) I and III **(D)** II, III and IV

***43.** The geometry and the type of hybrid orbital present about the central atom in BF_3 is :
(A) linear, sp **(B)** trigonal planar, sp^2
(C) tetrahedral, sp^3 **(D)** pyramidal, sp^3

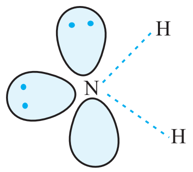
***44.** SF_2, SF_4 and SF_6 have the hybridisation at sulphur atom respectively as :
(A) sp^2, sp^3, sp^2d^2 **(B)** sp^3, sp^3, sp^3d^2
(C) sp^3, sp^3d, sp^3d^2 **(D)** sp^3, spd^2, d^2sp^3

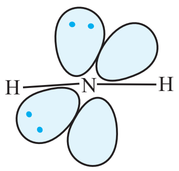
45. Two types FXF angles are present in which of the following molecule (X = S, Xe, C)
(A) SF_4 **(B)** XeF_4
(C) SF_6 **(D)** CF_4

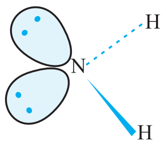
46. Which is not the correct order for the stated property ?
(A) Ba > Sr > Mg ; atomic radius
(B) F > O > N ; first ionization enthalpy
(C) Cl > F > I ; electron affinity
(D) O > Se > Te ; electronegativity

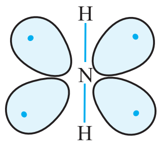
47. Which is correct statement about diborane structure ?
(A) All HBH bond angles are equal
(B) All H-B bond lengths are equal
(C) It has two three-centre-2 electron bonds
(D) All hydrogens and boron atoms are in one plane

48. For $\bar{N}H_2$, the best three-dimensional view is :

(A)


(B)


(C)


(D)


49. In which pair of species, both species do have the similar geometry ?

(A) CO_2, SO_2 **(B)** NH_3, BH_3

(C) CO_3^{2-}, SO_3^{2-} **(D)** SO_4^{2-}, ClO_4^-

50. In which of the following arrangements, the sequence is not strictly according to the property written against it ?

(A) $NH_3 < PH_3 < As\ H_3 < SbH_3$: increasing basic strength

(B) $B < C < O < N$: increasing first inoization enthalpy

(C) $CO_2 < SiO_2 < SnO_2 < PbO_2$: increasing oxidising power

(D) $HF < HCl < HBr < HI$: increasing acid strength

51. Which of the following substances has the highest melting point ?

(A) NaCl **(B)** KCl

(C) MgO **(D)** BaO

52. Which of the following statement is correct ?

(A) $FeCl_2$ is more covalent than $FeCl_3$

(B) $FeCl_3$ is more covalent than $FeCl_2$

(C) Both $FeCl_2$ and $FeCl_3$ are equally covalent

(D) $FeCl_2$ and $FeCl_3$ do not have any covalent character

53. Which one of the following compounds has sp^2-hybridisation ?

(A) CO_2 **(B)** SO_2

(C) N_2O **(D)** CO

Subjective Type :

54. Draw structures of following species.

(a) SbF_4^- **(b)** SF_5^- **(c)** SeF_3^+ **(d)** SOF_4 **(e)** ClO_2F_3 **(f)** XeO_3F_2 **(g)** HCP **(h)** IOF_4^- **(i)** $SeOCl_2$
(j) $XeOF_2$ **(k)** $ClOF_3$ **(l)** $SOCl_2$ **(m)** COF_2 **(n)** SNF_3 **(o)** XeO_3 **(p)** IOF_5 **(q)** IOF_3 **(r)** $XeOF_4$

MOLECULAR ORBITAL THEORY

Section - 3

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).