(c) The π bond is cylindrical whereas σ bond is not.

(d) There will be maximum electron density along the bond axis in case of σ bond whereas in case of π bond there will be small electron density along the surface of the cylinder.

(e) σ bonds determine the geometry of a molecule whereas π bond is not.

(f) In all chemical reactions π bond will take part first then σ bond.

(g) Free rotation about C–C σ bond is permitted but rotation about C=C or C≡C is restricted.

(h) A σ bond has cylindrical symmetry along the bond axis whereas π bond possess a plane of symmetry often called as the nodal plane.

~~Eq~~

Equivalent and non-equivalent hybrid orbitals

Generally hybrid orbitals are equivalent e.g sp, sp², sp³ etc, but there are certain hybrid orbitals which are nonequivalent. Equivalent hybrid orbitals results when the percentage contribution of individual atomic orbitals are the same in all the hybrid orbitals. ~~results~~ In sp, sp² and sp³ hybrid orbitals the percentage of s orbital contribution is 50, 33 and 25 percent respectively in all the 2 hybrid orbitals of sp, in all the 3 hybrid orbitals of sp² and in all the 4 hybrid orbitals of sp³ respectively.

But in case of sp³d or dsp³ the five bonds are not equivalent — the three equivalent hybrid orbitals ~~ofs~~ formed between $(s+p_x+p_y)$ lie in the xy equatorial plane which are at 120° apart and the other two equivalent hybrid orbitals formed between the overlap of $(p_z + d_{z^2})$ directed mutually 180° in the axial directions i.e perpendicular to the xy plane. The equatorial bonds has s orbital contribution but axial bonds has no s character and so the axial and equatorial bonds are called nonequivalent hybrids. e.g PCl_5. In this ~~tha~~ three equatorial P-Cl bonds are shorter (2·04A°) than the two axial P-Cl bonds (2·19A°) having trigonal bipyramidal (TBP) geometry of PCl_5. Therefore this hybridisation can be split into sp^2 for the three equatorial bonds and dp for two axial bonds.

Five coordination can also be achieved through d^2sp^2 and sp3d hybridisation having square pyramid (SP) geometry e.g. $[VO(acac)_2]$ where acacH = acetylacetone. Here in sp^3d process the combination can be represented as $s + p_x + p_y + d_{x^2-y^2}$ which forms four sp^2d equivalent equatorial bonds in the xy plane and the fifth one is the pure p_z orbital lying perpendicular to the xy plane ~~and the fifth one is~~ (axial bond).

In AX_5 molecule the energy difference between TBP and SP geometries are small so that there may be an equillibrium between the two geometries i.e TBP $\rightleftharpoons$ SP. For this reason there are some molecular species e.g. $CdCl_5^{3-}$, $Ni(CN)_5^{3-}$ etc. may exist in both the configurations.

Where the hybrid orbitals may be equivalent (tetrahedral sp3) or nonequivalent (trigonal bipyramid or square pyramid sp3d) will be dictated by the electronegativity difference of the central atom with that of the combining atoms. The equivalence of the hybrid orbitals are lost in some cases where some of the hybrid orbitals are occupied by lone pairs. In CH_4 and CH_3Cl the central atom C in both the cases is sp3 so that in case of CH_4 the four hybrid orbitals are equivalent having identical tetrahedral angle 109°28'. But in case of CH_3Cl the bond angle H-C-H is 110° which is somewhat different from bond angle H-C-Cl. This variation in bond angle is explained by Bent's rule. This difference in bond angles attributed by the uniform distribution of s and p character of different atomic orbitals in the bonding orbitals. The three hybrid orbitals of carbon that overlap with hydrogen has slight higher s character making higher bond angle (110°). The fourth hybrid orbital of carbon that overlaps with p orbital have slightly s character making lower bond angle. In general, for ~~an~~ combination of s and p, with the increase of p character, the bond angle decreases. In NH_3 and H_2O, the central element nitrogen and oxygen respectively is sp3 hybridised and the bond angles are 107° and 104° respectively.

3.2.7 Aspects of hybridisation in terms of wave mechanics

LCAO in hybridisation

The orbital wave functions undergo a linear combination to form hybrid orbitals like that in case of molecular orbitals. The difference between hybrid orbitals and molecular orbitals is that in case of hybrid orbitals it involves between orbitals of same atom whereas in case of molecular orbitals, LCAO involves between different atoms.

The basic approach of covalent bonding is the overlap of atomic orbitals—the shapes and sign of the wave functions must be such that the two atomic orbitals have positive overlap. In order to form hybrid orbitals overlap, the involving atomic orbitals **should not differ significantly in the radial parts of their wave functions**. On the other hand for effective hybridisation, the combining atomic orbitals should have comparable magnitude of energy. Hybridised orbitals can be constructed from the angular parts of the individual wave functions. We shall consider some salient feature of hybridisation :

(a) Hybrid orbital concept represents better overlap properties than do the pure s, p and d orbitals. For example the s and p orbital of the same atom can be mixed or hybridised to produce new **sp hybrid orbital** (Fig. 3.9) combination of crest (positive lobe) of s orbital with p orbital with its crest to the right produces sp hybrid orbital with most of the probability of finding the electron at the right [Fig. 3.9(a)]. On the other hand other possible combination of the same orbitals produces maximum overlap represented to the left [Fig. 3.9(b)]. In a similar way other hybrid orbitals can also be represented (Fig. 3.10).

Energetics of hybridisation

(b) One or more electrons from fully filled orbitals of the atom in the ground state, will be promoted to the next available orbitals of higher energy resulting in an excited state electronic configuration. This requires energy. The orbitals in the excited state then undergo hybridisation to form equivalent hybrid orbitals. The energy difference between the unhybridised atomic orbitals and the hybridised atomic orbitals is known as **energy of hybridisation** (E_{hy}). The E_{hy} gives a measure to carry out the process of hybridisation. Hence for an effective hybridisation to occur, the entire input of energy is more than recovered than

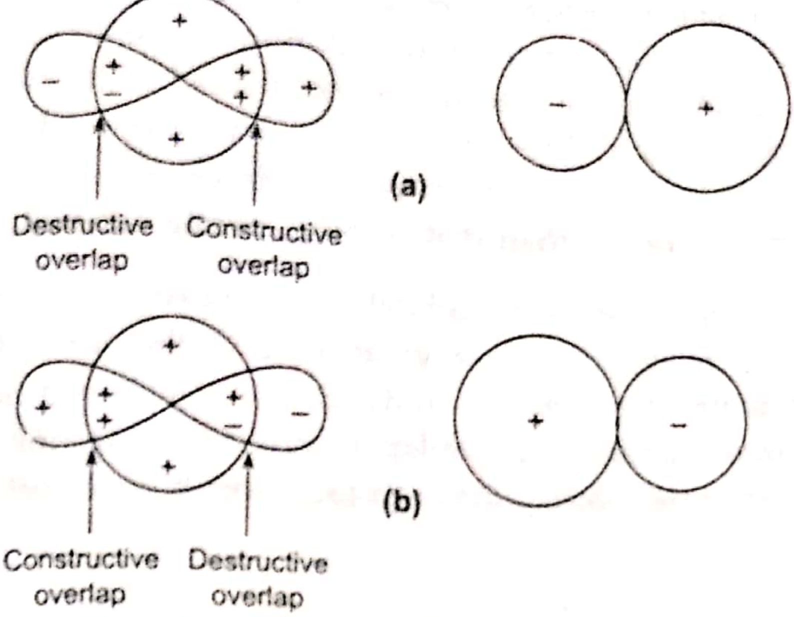


Figure 3.9 : Pictorial representation of overlap of s and p orbital to form sp hybrid orbitals.

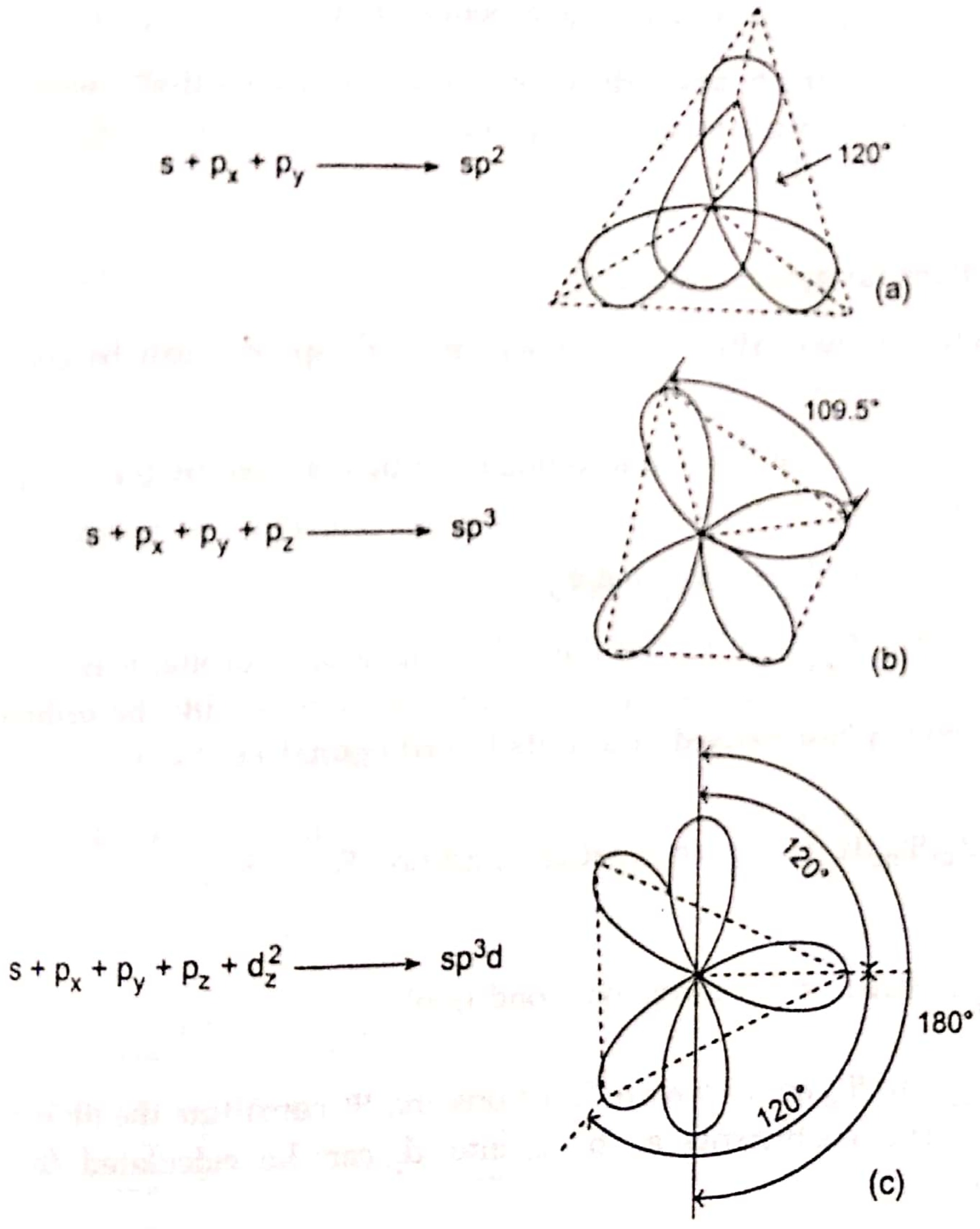


Figure 3.10 : The shapes of different types of hybrid orbitals (a) sp^2, (b) sp^3, (c) sp^3d.

the E_{ex} when the hybrid orbitals combine with the orbitals of other atoms to form covalent bonds. Thus the energy released during covalent bond formation involving hybrid orbitals is much more than the energy relased if the covalent bond is formed from pure atomic orbitals. Therefore covalent bonds formed by hybrid orbitals are more stable than those formed by pure atomic orbitals so that **atoms prefer to combine with hybrid orbitals rather than that of pure atomic orbitals.**

(c) Bonding potentiality of the hybrid orbitals are dictated by the angular strength of the orbitals which is related to the angular part of the wave function. s orbital is spherically symmetrical whereas p orbital is dumbell shaped having greater angular orientation is most suitable for overlap in projected direction. Angular strength of orbitals is related to the overlap integrals (S_{AB}) which are directed in proper direction of the hybrid orbitals.

(d) The number of hybrid orbitals are equal to the number of participating atomic orbitals.

(e) Hybridisation occurs between the orbitals of the same atom.

(f) Hybrid orbitals generally form sigma bonds or contain lone pair of electrons.

(g) As s character of the hybrid orbitals increases, electronegativity increases ($sp > sp^2 > sp^3$). Bond angle increases with increasing s character ($sp^3 < sp^2 < sp$) but decreases with increasing p character.

Prediction of type of hybridisation in some molecules

The structure of a molecule can be predicted on the basis of hybridisation. The type of hybridisation can be known by the following general formula:

$$N = \frac{1}{2}\left[\begin{array}{l}\text{No. of electrons}\\ \text{in the valence}\\ \text{shell}\end{array} + \begin{array}{c}\text{No. of}\\ \text{monovalent}\\ \text{atoms.}\end{array} - \begin{array}{c}\text{Charge}\\ \text{on}\\ \text{Cation}\end{array} + \begin{array}{c}\text{Charge}\\ \text{on anion}\end{array}\right]$$

or $N = \frac{1}{2}\left[V + M - C + A\right]$ $\left[N = \text{No. of orbitals hybridised}\right]$

L = Lone pair of electrons = N − M − D

· D is the no. of divalent atoms.

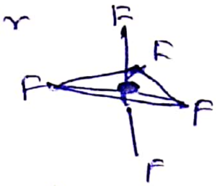
value of N :	2	3	4	5	6	7
Hybridisation :	sp	sp^2	sp^3	sp^3d	sp^3d^2	sp^3d^3

Egs: Type 1: Central atom is surrounded by monovalent atoms only e.g. BeF_2, BCl_3, CH_4, PCl_5, PCl_3, H_2O, NH_3, $TeCl_4$, SCl_2, ClF_3, SF_4, XeF_2, XeF_4, SF_6 etc.

① PF_5 : $N = \frac{1}{2}[5+5-0+0] = 5 \Rightarrow sp^3d$ hybridisation

$L = 5-5-0 = 0 \Rightarrow$ No lone pair

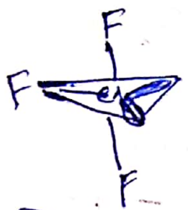
∴ shape trigonal bipyramid



② ClF_3 : $N = \frac{1}{2}[7+3-0+0] = 5 \Rightarrow sp^3d$ hybridisation

$L = 5-5-0 = 0 \Rightarrow$ No lone pair

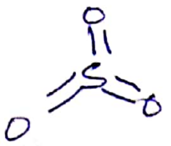
shape trigonal bipyramid. (T-shaped.)



Practice Yourselves: Other compounds in the above list.

Type 2: Central atom is surrounded by divalent atoms only eg SO_2, CO_2, CS_2, XeO_3, SO_3 etc.

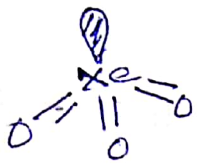
e.g.① SO_3: $N = \frac{1}{2}[6+0-0+0] = 3 \Rightarrow sp^2$ hybridisati



$L = 3-0-3 = 0 \Rightarrow$ No lone pair

Shape: Trigonal Planar

② XeO_3: $N=\frac{1}{2}[8-0-0+0] = 4$



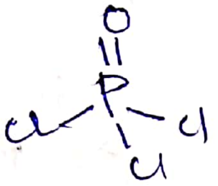
$L = 4-0-3 = 1$ (one lone pair)

shape Tetrahedral

~~Pr~~actice Yourselves: Other above listed compounds

Type3: Central atom is surrounded by monovalent as well as divalent atoms. Eg: $COCl_2$, $XeOF_2$, XeO_2F_2, $XeOF_4$, $POCl_3$ etc.

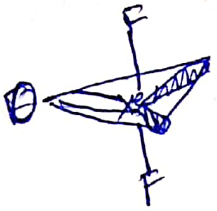
e.g. $POCl_3$: $N = \frac{1}{2}[5+3-0+0]=4 \Rightarrow sp^3$



$L=4-3-1 = 0 \Rightarrow$ No lone pair

Shape: Tetrahedral

$XeOF_2$: $N = \frac{1}{2}[8+2-0+0] = 5 \Rightarrow sp^3d$



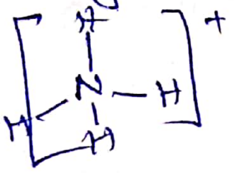
$L=5-2-1 = 2 \Rightarrow$ Two lone pairs

Shape: Trigonal bipyramid

Practice other compounds

Type IV: Hybridisation in Cations
e.g. NH_4^+, CH_3^+, H_3O^+ etc.

e.g NH_4^+: $N=\frac{1}{2}[5+4-1+0] = 4$



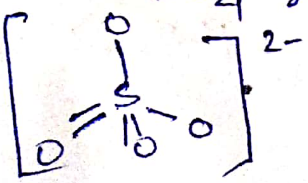
$L = 4-4=0$ (No lone pair)

Shape: Tetrahedral

Others are for yours Practices.

Type 5: Hybridisation in anions
e.g. CO_3^{2-}, NO_2^-, NO_3^-, SO_4^{2-}, PO_4^{3-}, ClO_3^-, ClO_4^- etc.

SO_4^{2-}: $N = \frac{1}{2}[6+0-0+2] = 4 \Rightarrow sp3$



$L = 4-0-4=0 =$ No lone Pair

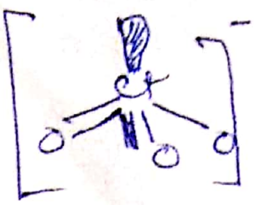
shape: Tetrahedral

ClO_3^- : $N = \frac{1}{2}[7+0-0+1] = 4 \Rightarrow sp^3$

$L = 4-0-3 = 1$ (one lone pair)

Shape: Tetrahedral

Practice others



Type VI: Hybridisation in complex ions

eg $I_3^-, ICl_2^-, ICl_4^-, ClF_2^-$ etc.

ICl_4^- : $N = \frac{1}{2}[7+4-0+1] = 6 \Rightarrow sp^3d^2$

$L = 6-4 = 2 \Rightarrow$ Two lone pairs

Practice others.

Bent's rule - Electronegativity and hybridisati

Non equivalent hybrid orbitals result from the axial and equatorial bonds around the central atom. Nonequivalence of the bonds may arise also when the central atom is joined to different elements having different electronegativity e.g. $CHCl_3$ and CH_3Cl. In CH_3Cl the ∠H–C–H = 110° and is different from ∠Cl–C–H. In case of $CHCl_3$ the ∠Cl–C–Cl = 110° which has a difference of bond angle of ∠Cl–C–H. This small variation of bond angles can be explained on the basis of the s and p character of hybrid orbitals. In the molecules $CHCl_3$ and CH_3Cl the central Carbon is joined to chlorine and hydrogen which have appreciable difference in electronegativity and thereby all the hybrid orbitals (sp^3) are not equivalent. Bent's rule gives us an idea why in the case of isovalent hybridisation all the hybrid orbitals are not equivalent.

Bent's concept can be stated as:

(a) When an electronegative atom bound to the central atom, this will pull more electron density from the central atom.

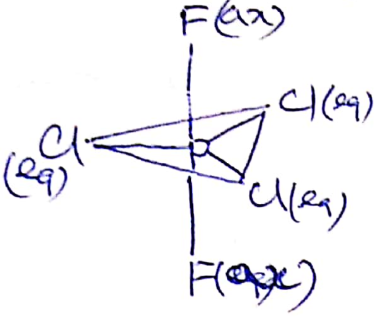
(b) The greater the p character of the hybrid orbital less will be the electronegativity. Conversely the hybrid orbital having more s character is more electronegative.

(c) The more electronegative substituents prefer those hybrid orbitals which have less s character while less electronegative or more electropositive substituents prefer hybrid orbitals with more s character.

(d) The central atom direct less p character and greater s character, into the hybrids directed towards less electronegative substituents.

The illustration of Bent's rule can be made in the case of nonequivalent hybrid e.g. PCl_5 where the central P is sp^3d hybridised. This hybridisation is a combination of sp^2 and pd hybridisation. The sp^2 forms trigonal planar equatorial bonds whereas pd forms perpendicular axial bonds.

In case of mixed halides such as PCl_3F_2, the fluorine is more electronegative than chlorine. Therefore fluorine will occupy those hybrid orbital which ~~too~~ has less s character i.e pd hybrid orbitals so that two F atoms will occupy in the axial positions. Cl is less electronegative than F so three Chlorine atoms will occupy the hybrid orbitals which has more s character i.e sp^2 hybrid orbitals so that three Cl atoms will be in equatorial directions. $\angle FPF = 180^0$ whereas $\angle ClPCl = 120^0$. The variation of s and p character of different s-p type hybrid orbitals are as follows:



Hybridisation	Percentage character		Bond angle
	s	p	
sp	50	50	180^0
sp^2	$33\frac{1}{3}$	$66\frac{2}{3}$	120^0
sp^3	25	75	$109^0 28'$
p^2	0	100	90^0

So the greater the s character greater is the bond angle while greater p-character indicated smaller bond angle.

The variation of bond angle in NH_3 and H_2O can be explained by this rule.

In NH_3, $\angle HNH = 107^0$

In H_2O, $\angle HOH = 104^0$

This difference in bond angle is due to the nonuniform distribution of s and p character of the bonding and nonbonding hybrid orbitals.

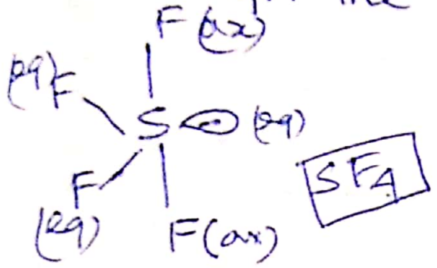
In both the cases the central atom N and O is sp^3 hybridised. so that the ideal bond angle should be $109^\circ 28'$.

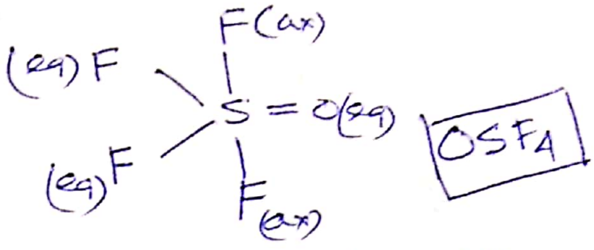
In H_2O, there is a reduction of about 5° angle whereas in NH_3 this angle is reduced to about 2°. The percentage of s character calculated in two adjacent O-H bonds is about 20% and that in NH_3, the adjacent three N-H bonds has ~22% character. Thus in NH_3 the bond angle will be higher than that of H_2O. Oxygen is more electronegative than nitrogen and so oxygen will have to combine with hybrid orbital having less s character while nitrogen ~~and~~ will have a tendency to combine with orbital having more s character. S orbital tend to attract less electronegative substituents or more electronegative substituents tend to get towards those orbitals which have lesser ~~tency~~ tendency to withdraw electrons. This tendency of more electronegative substituents to seek out orbitals with less s character is called apicophilicity.

In OSF_4, the axial $\angle FSF = 164^\circ$ which is just 16° less than the ideal 180° angle while the eqatorial $\angle FSF = 115^\circ$ which is quite close to the ideal angle 120°.

In SF$_4$, the axial ∠FSF = 173° which is 7° reduced from the ideal angle 180°. The equatorial ∠FSF = 101° which is about 19° reduced from the ideal angle 120°. (which is expected by the l.p and b.p. repulsion according to VSEPR theory).

The ~~x~~explanation according to Bent's rule for the above observation is as follows:





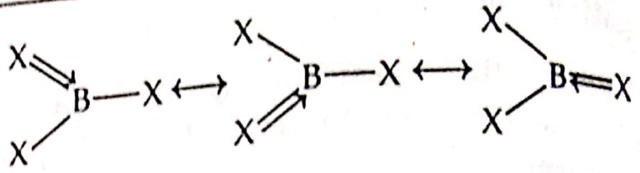
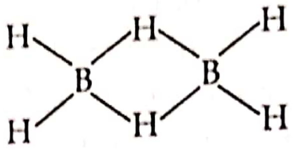
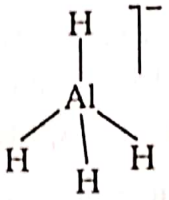
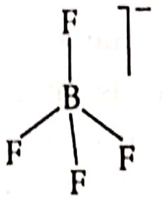
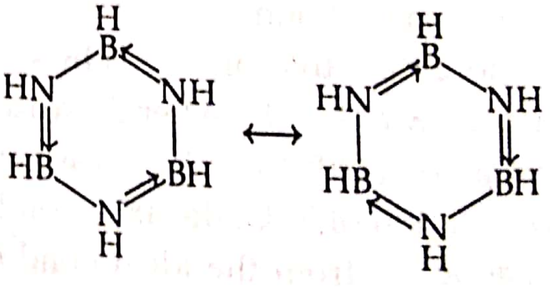
The lone pair in SF$_4$ is under the control of a single nucleus which is considered to have the ~~effective~~ electronegativity zero. So it is more likely that this lone pair will attract the more s character than than the equatorial bond pairs. Therefore the p-character in equatorial bond pairs, will be ~~\$~~ more than that predicted by sp^2 hybridisation, thereby we expect greater decrease of equatorial bond angle (~~120~~ 120° to 101°). In case of OSF$_4$ due to the formation of S=O, the axial bond angle decreases about 16° from the ideal bond angle which is quite plausible that the double bond will exert greater repulsive force. But the equatorial bond angle is quite close to 120° which is expected from bent's rule. This is considered as the substitution of the lone pair in SF_4 by double bonded oxygen in OSF_4. As oxygen is more electronegative than lone pair, so p character will predominate than s character so that equatorial bonds will be more closer to sp^3 in OSF_4 than SF_4. Hence the equatorial bond angles are quite close to the ideal bond angle for sp^3 hybridisation.

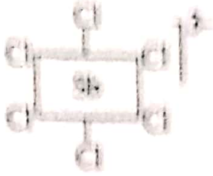
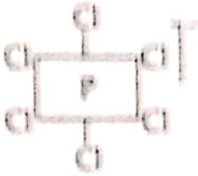
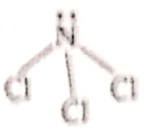
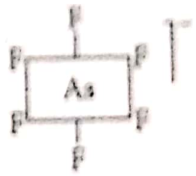
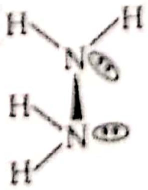
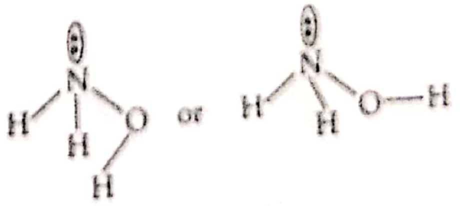
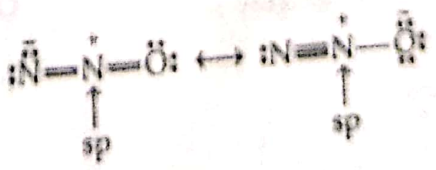
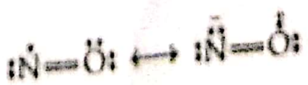
The variation of equatorial and axial bond angles in several cases can be explained by the application of bent's rule e.g. in ClF_3 ~~to~~ two lone pairs and one F occupy equatorial positions while two other fluorines occupy axial positions. The ∠F Cl F is slightly lower than ideal 90°. In $OClF_3$ the equatorial ∠O Cl F = 109° which is shorter than expected 120°.

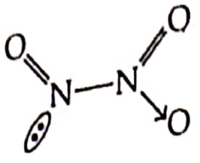
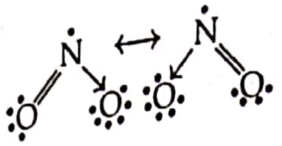
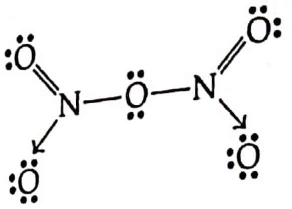
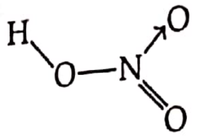
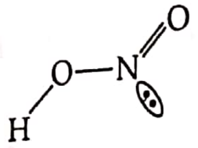
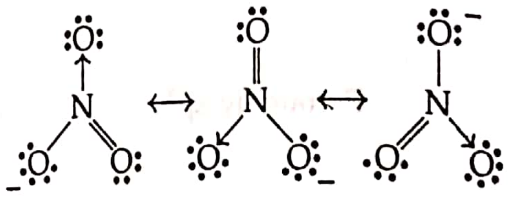
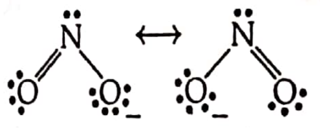
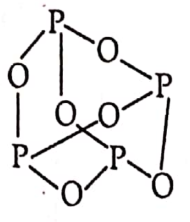
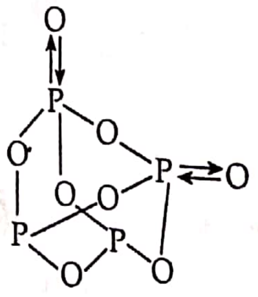
Valence Shell Electron Pair Repulsion Model (VSEPR)

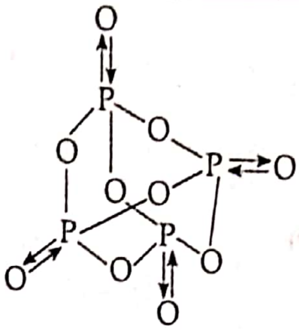
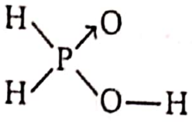
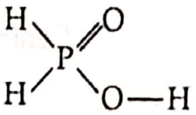
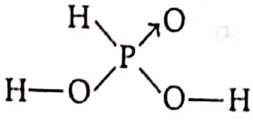
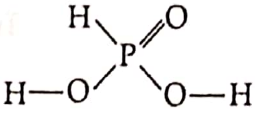
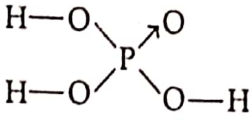
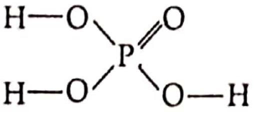
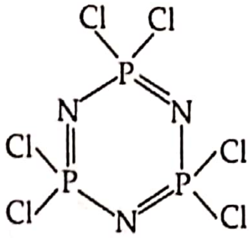
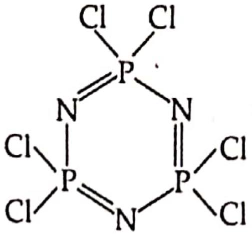
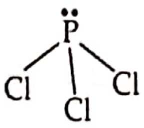
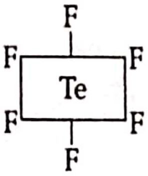
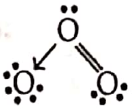
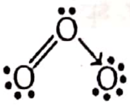
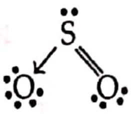
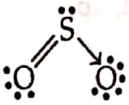
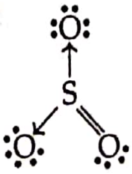
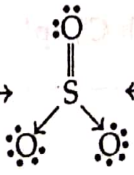
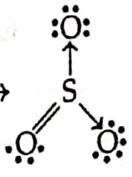
According to this model shapes of molecules or ions are determined by the repulsion of valence shell pair of electrons i.e. by the electrostatic repulsions of the negatively charged

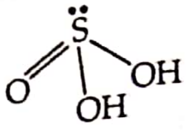
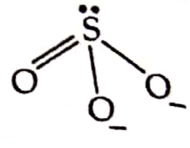
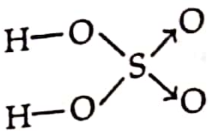
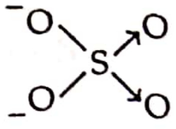
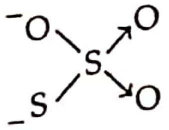
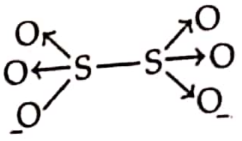
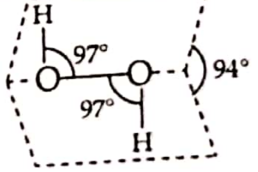
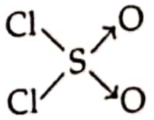
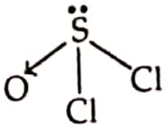
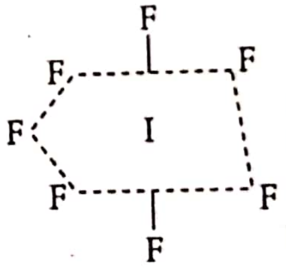
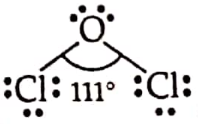
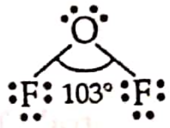
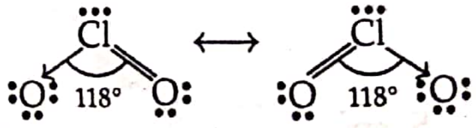
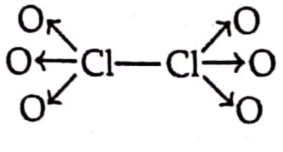
Table 3.7 : Hybridisation of the central element the structure of some molecular species

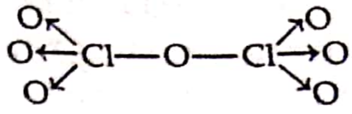
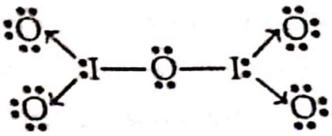
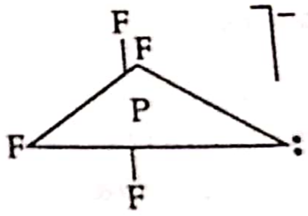
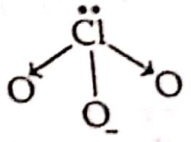
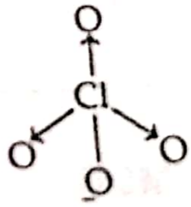
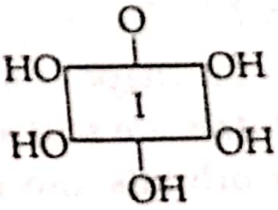
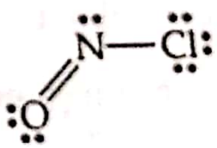
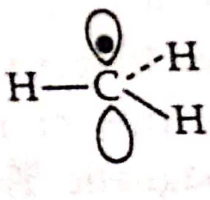
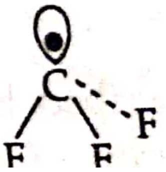
Molecular species	Hybridisation of the central element	Structure
BX_3(X=F, Cl)	B, sp^2	
$BeCl_2$	Be, sp	Cl—Be—Cl
B_2H_6	B, sp^3	
AlH_4^-	Al, sp^3	
BF_4^-	B, sp^3	
$B_3N_3H_6$ (Inorganic benzene)	B and N, sp^2	
BN (Inorganic graphite)	B and N, sp^2	Graphite like structure
CO	C, sp	:C$\equiv$O:
CO_2	C, sp	O=C=O

Molecular species	Hybridisation of the central element	Structure
$(CN)_2$	C and N, sp	$N\equiv C-C\equiv N$
$[SbCl_6]^{3-}$	Sb, sp^3d^2	
$[PCl_6]^-$	P, sp^3d^2	
NCl_3	N, sp^3	
$[AsF_6]^-$	As, sp^3d^2	
N_2	N, sp	$:N\equiv N:$
P_4	P, roughly sp^3	
O_2	O, sp	$:\ddot{O}=\ddot{O}:$
N_2H_4	N, sp^3	
NH_2OH	N, sp^3	
N_2O	N, sp	
NO	N, sp	

Molecular species	Hybridisation of the central element	Structure
N_2O_3	N, sp^2	
NO_2	N, sp^2	
N_2O_5	Both N is sp^2, O is sp	
HNO_3	N, sp^2	
HNO_2	N, sp^2	
NO_3^-	N, sp^2	
NO_2^-	N, sp^2	
P_2O_3 or P_4O_6	P, roughly sp^3	
P_2O_4 or P_4O_8	P, roughly sp^3	

Molecular species	Hybridisation of the central element	Structure
P_2O_5 or P_4O_{10}	P, roughly sp^3	
H_3PO_2	P, sp^3	 or 
H_3PO_3	P, sp^3	 or 
H_3PO_4	P, sp^3	 or 
$(PNCl_2)_3$	P roughly sp^3, N is sp^2	 ↔ 
PCl_3	P, sp^3	
TeF_6	Te, sp^3d^2	
O_3	Central O, sp^2	 ↔ 
SO_2	S, sp^2	 ↔ 
SO_3	S, sp^2	 ↔  ↔ 

Molecular species	**Hybridisation of the central element**	**Structure**
H_2SO_3 or SO_3^{2-}	S, sp^3	 or 
H_2SO_4 or SO_4^{2-}	S, sp^3	 or 
$S_2O_3^{2-}$	Central S, sp^3	
$S_2O_6^{2-}$	Two S, sp^3	
H_2O_2	—	Open book structure 
SO_2Cl_2	S, sp^3	
$SOCl_2$	S, sp^3	
IF_7	I, sp^3d^3	 (Pentagonal bipyramid)
Cl_2O, F_2O	O, sp^3	 
ClO_2	Cl, sp^3	
Cl_2O_6	Each Cl, sp^3	

Molecular species	Hybridisation of the central element	Structure
Cl_2O_7	Each Cl, roughly sp³	 terminal ∠OClO = 115° bridging ∠ClOCl = 119°
I_2O_5	Each I sp², bridging O sp	
PF_4^-	P, sp³d	
ClO_2^-	Cl, sp³	$O—Cl\rightarrow O]^-$
ClO_3^-	Cl, sp³	
ClO_4^-	Cl, sp³	
H_5IO_6	I, sp³d²	
NOCl	N, sp²	
$\dot{C}H_3$	C, sp²	
$\dot{C}F_3$	C, sp³	

covalent bond electron pairs and lone pairs of hybridised valence electrons about the central atom. Valence Shell Pair of Electrons means the total pair of electrons in the valence shell of central atom i.e the total number of electrons in the valence shell plus the number of electrons gained by the central atom.

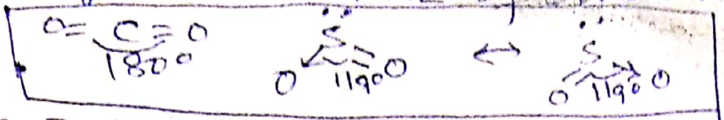
Valence shell electron pairs are arranged around the central atom in such a way that the repulsion will be minimum and the regions of high electron density will maximize their distance apart. For example, two regions of high electron density are most stable on the opposite side of the central atom giving a linear arrangement. ~~These~~ Three regions of space of high electron density at the corners of an equilateral triangle giving a triangular planar arrangement. Thus the arrangement of regions of high electron density will dictate the geometry of a molecule.

VSEPR theory yields qualitative results and when unshared electron pairs are present this model predict slight deviation of bond angle from ideal geometry. The deviation of bond angle with different coordination number with the number of number of bonds with different geometries having different number of unshared paired of electrons reveals that unshared electron pairs occupy more space about the central atom that an electron pair shared with an outer atom. When the lone pair repulsions are balanced on all sides of a given bond pairs as in the case of XeF_2, an undistorted bond angle is retained.

In VSEPR theory, it is assumed that inner electrons of the central element will not take part in valence shell repulsion and this theory provide the idea of geometries of molecules of non-transition elements as also symmetrical transition metals (d^0, d^5 and d^{10} systems) having no CFSE. The refinement of bond angles due to lone pair - bond pair repulsion is governed by certain rules:

Rule 1: Molecular species having no lone pair (lp) of electrons on the central atom will not exert repulsive force and the number of σ bonding pairs will determine the ideal geometry of the concerned species. π bonding pairs will not influence the geometry of the system.

In CO_2 there is no lone pair, so ideal geometry (linear) having regular bond angle 180° is retained but in case of SO_2 there is one lp on central S and so due to lone pair - bond pair repulsion there will be slight deviation of bond angle from 120° to 119°.



Rule II : Lone pair of electrons repel the neighbouring electron pairs more strongly than bond pair of electrons and the sequence of repulsion is:
lone pair(lp) – lone pair (lp) > lone pair (lp)–bond pair(bp) > bond pair(bp) - bond pair (bp).

As for e.g.: CH_4 (109°28′), NH_3(107°), H_2O(104°)
In CH_4 : only b.p-bp repulsion which is minimum
In NH_3 : one l.p. so 3 (lp-bp repulsion) and 3(bp-bp repulsion) ⇒ 107°
In H_2O : two l.p. so 1 (lp-lp), 4 (lp-bp), 1 (bp-bp) ⇒ 104°

Rule II : Repulsion exerted by the bp decreases as the electronegativity of the B atom increases in a AB_n type of species where A is the central atom and n is the number of atoms attached to A. This can be stated as BAB bond angle decreases with increasing electronegativity of B.

With increasing electronegativity of the B atom the bond pair electron density is pulled further from the central atom A and the charge cloud is displaced further away from the central atom causing more decrease of bond angles.

Eg: NH_3 107° ; NF_3 102° ; H_2O 104° ; OF_2 103°

The same effect is also observed for decreasing size of the B atom of the same group

Eg. PF_3 98°, PCl_3 100°, PBr_3 101·5°, PI_3 102°

$AsCl_3$ 98°, $AsBr_3$ 100°, AsI_3 101°

With increasing electronegativity of the central atom, the bonding electron pairs [illegible] ~~Centr~~ are more concentrated around the central atom causing expansion of bond angle and hence the sequence of bond angle:

$H_2O > H_2S > H_2Se > H_2Te$

$NH_3 > PH_3 > AsH_3 > SbH_3$

Rule IV: Repulsion between electron pairs in filled shell is more than the repulsion between electron pairs in incompletely filled shell.

Though the repulsion is less in incompletely filled shell yet due to the greater flexibility of bonds due to more space available for central atom, the deviation of bond angle from ideal behaviour is more compared to the filled shell. In filled shell there will be greater rigidity of the bonds due to smaller space available for central atom which causes small deviation of bond angle from ideal behaviour.

H_2O 104°, H_2S 92° NH_3 107° PH_3 93°

Oxygen and nitrogen has filled shell (n=2) whereas ~~and~~ S and P has incompletely filled shell (n=3) which has the availability of 3d orbitals. This causes quenching of bond angles dramatically from ideal behaviour (109°) to 92° and 93° in PH_3.

Rule 2: Multiple bonds do not grossly influence the geometry of a molecular species. σ bonding pair dictates the geometry of a molecule. Multiple bonding i.e. σ and π bonding together exert stronger repulsive force on the neighbouring electron pair than a single σ bond does thereby causing smaller bond angles as expected from the ideal geometry.

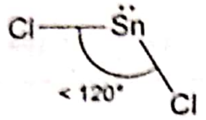
Eg: $O=PF_3$	$\angle FPF = 102{\cdot}5^\circ$	$O=CF_2$ $\angle FCF = 108^\circ$
$O=PCl_3$	$\angle ClPCl = 103{\cdot}5^\circ$	$O=CCl_2$ $\angle ClCCl = 111^\circ$
$O=PBr_3$	$\angle BrPBr = 108^\circ$	$O=CMe_2$ $\angle MeCMe = 119{\cdot}6^\circ$

In the case of OPX_3 molecules having tetrahedral geometry the ideal bond angle is 109° whereas in case of OCX_2 molecules the expected bond angle is 120° having triangular planar geometry. In both the cases large deviation occurs in case of fluorine. Due to the highest electronegativity of fluorine which pulls the bond pair of electrons farthest from P and C and thereby bp-bp repulsion minimizes whereby repulsion of the double bond makes the $\angle FPF$ and $\angle FCF$ least.

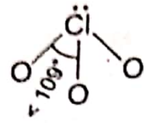
Limitations of VSEPR model:

(a) This model cannot provide quantitative result of bond angles.

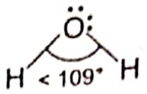
(b) This theory is not applicable in case of molecules having fluxional behaviour i.e. for stereochemically non-rigidity character of a molecule like XeF_6. Those molecules that have more than one equivalent minimum-energy conformation and that are readily able to change from one conformation to other, are called fluxional molecules. (c) It fails to explain the geometry of transition metal complexes where the CFSE plays a pivotal role in structure determination.



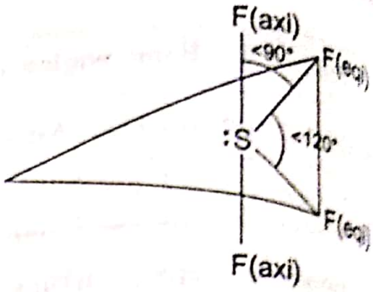
1 lone pair, total number of bonds = 3, actual bonds = 2, bent geometry



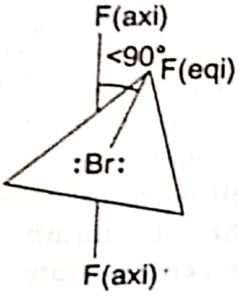
1 lone pair, total number of bonds = 4, actual bonds = 3, pyramidal geometry



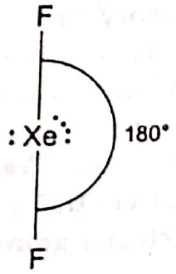
2 lone pairs, total number of bonds = 4, actual bonds = 2, bent geometry



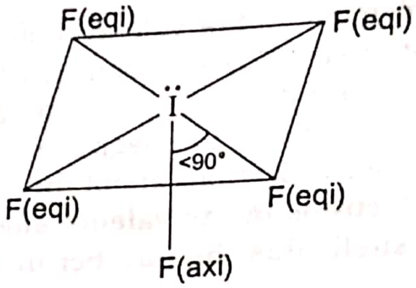
1 lone pair, total number of bonds = 5, actual bonds = 4, distorted tetrahedral geometry



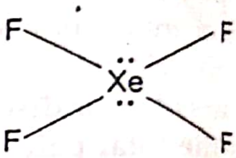
2 lone pairs, total number of bonds = 5, actual bonds = 3, T-shaped geometry



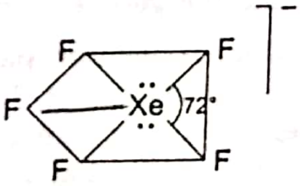
3 lone pairs, total number of bonds = 5, actual bonds = 2, linear geometry



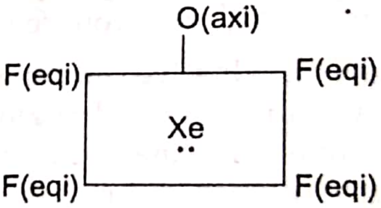
1 lone pair, total number of bonds = 6, actual bonds = 5, square pyramidal geometry



2 lone pairs, total number of bonds = 6, actual bonds = 4, square planar geometry



2 lone pairs, total number of bonds = 7, actual bonds = 5, pentagonal planar geometry



1 lone pair, total number of bonds = 6, actual bonds = 5, square pyramidal geometry

***Figure 3.15** : Distortions of bond angle due to lone pair of electrons in different geometries. axi = axial, eqi = equatorial*

The shapes of some typical molecules according to VSEPR model are given in Table 3.6.

Table 3.6 : Geometry of some molecules having lone pair of electrons

Type of molecules	Hybridisation and distribution of orbitals	Types of electron pairs	Actual shape	Example
AB_2	sp^2, triangular planar	2 b.p. + 1 *l*.p.	V-shaped (bent)	$SnCl_2$, $PbCl_2$, SO_2
	sp^3, tetrahedral	2 b.p. + 2 *l*.p.	V-shaped (bent)	H_2O, F_2O, Cl_2O, NO_2^-, XO_2^-, (X=Cl, Br, I)
	sp^3d, trigonal bipyramid	2 b.p. + 3 *l*.p.	Linear	XeF_2, ICl_2^-, I_3^-
AB_3	sp^3, tetrahedral	3 b.p. + 1 *l*.p.	Trigonal pyramid	NH_3, NF_3, SO_3^{2-}, H_3O^+ PX_3, XeO_3, XO_3^-, (X=Cl, Br, I)
	sp^3d, trigonal bipyramid	3 b.p. + 2 *l*.p.	T-shaped	ClF_3, BrF_3
AB_4	sp^3d, trigonal bipyramid	4 b.p. + 1 *l*.p.	Distorted tetrahedral	$TeCl_4$, $TeBr_4$, SF_4, XeO_2F_2
	sp^3d^2, octahedral	4 b.p. + 2 *l*.p.	Square planar	XeF_4, ICl_4^-, BrF_4^-
AB_5	sp^3d^2, octahedral	5 b.p. + 1 *l*.p.	Square pyramid	IF_5, BrF_5, $XeOF_4$
	sp^3d^3, pentagonal bipyramid	5 b.p. + 2 *l*.p.	Pentagonal planar	XeF_5^-