



Chemical Bonding-II

Section (A) : VSEPR theory

Valence shell electron pair repulsion (VSEPR) theory :

Lewis concept is unable to explain the shapes of molecules. This theory provides a simple procedure to predict the shapes of covalent molecules. Sidgwick and Powell in 1940, proposed a simple theory based on the repulsive interactions of the electron pairs in the valence shell of the atoms. It was further developed and redefined by Nyholm and Gillespie (1957).

The main postulates of VSEPR theory are as follows :

- The shape of a molecule depends upon the number of valence shell electron pairs [bonded or nonbonded] around the central atom.
- Pairs of electrons in the valence shell repel one another since their electron clouds are negatively charged.
- These pairs of electrons tend to occupy such positions in space that minimise repulsion and thus maximise distance between them.
- The valence shell is taken as a sphere with the electron pairs localising on the spherical surface at maximum distance from one another.
- A multiple bond is treated as if it is a single electron pair and the two or three electron pairs of a multiple bond are treated as a single super pair.
- Where two or more resonance structures can represent a molecule, the VSEPR model is applicable to any such structure.

The repulsive interaction of electron pairs decreases in the order :

lone pair (lp) - lone pair (lp) > lone pair (lp) - bond pair (bp) > bond pair (bp) - bond pair (bp)

Nyholm and Gillespie (1957) refined the VSEPR model by explaining the important difference between the lone pairs and bonding pairs of electrons. While the lone pairs are localised on the central atom, each bonded pair is shared between two atoms. As a result, the lone pair electrons in a molecule occupy more space as compared to the bonding pairs of electrons. This results in greater repulsion between lone pairs of electrons as compared to the lone pair-bond pair and bond pair-bond pair repulsions. These repulsion effects result in deviations from idealised shapes and alterations in bond angles in molecules.

For the prediction of geometrical shapes of molecules with the help of VSEPR theory it is convenient to divide molecules into two categories as (i) molecules in which the central atom has no lone pair and (ii) molecules in which the central atom / ion has one or more lone pairs.

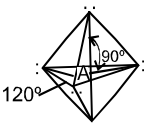
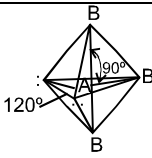

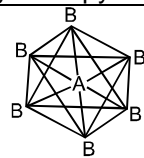
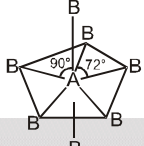
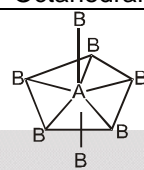
Shape (molecular geometry) of Some Simple Molecules / ions with central atom/ion having no Lone Pairs of Electrons (E).

Table-1

Number of electron pairs	General formula type	Arrangement of electron pairs	Molecular Geometry	Example
2	AB ₂	 Linear	B-A-B Linear	BeCl ₂ , HgCl ₂
3	AB ₃	 Trigonal planar	 Trigonal planar	BF ₃
4	AB ₄	 Tetrahedral	 Tetrahedral	CH ₄ , NH ₄ ⁺


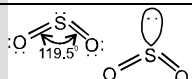

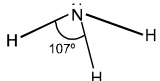

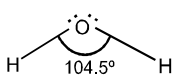

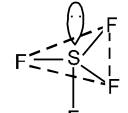

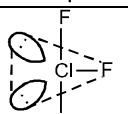
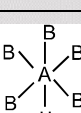
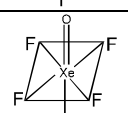
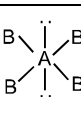
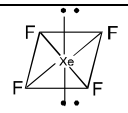
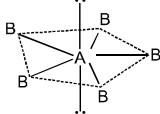
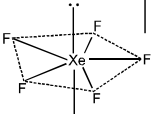




5	AB ₅	 <p>Trigonal bipyramidal</p>	 <p>Trigonal bipyramidal</p>	PCl ₅
6	AB ₆	 <p>Octahedral</p>	 <p>Octahedral</p>	SF ₆
7	AB ₇	 <p>Pentagonal bipyramidal</p>	 <p>Pentagonal bipyramidal</p>	IF ₇

Shape (molecular geometry) of Some Simple Molecules/Ions with central atom / ions having One or More Lone Pairs of Electrons (E).

Table-2

General formula type	No. of bonding pairs	No. of lone pairs	Arrangement of electron pairs	Shape	Examples
AB ₂ E	2	1		Bent	SO ₂ , O ₃ 
AB ₃ E	3	1		Trigonal Pyramidal	NH ₃ 
AB ₂ E ₂	2	2		Bent	H ₂ O 
AB ₄ E	4	1		See saw	SF ₄ 
AB ₃ E ₂	3	2		T-shape	ClF ₃ 
AB ₅ E	5	1		Square Pyramidal	XeOF ₄ 
AB ₄ E ₂	4	2		Square Planar	XeF ₄ 
AB ₅ E ₂	5	2		Pentagonal Planar	XeF ₅ ⁻ 

Shapes of Molecules containing Bond Pair and Lone Pair



Solved Examples

Ex-1. Use the VSEPR model to predict the geometry of the following :

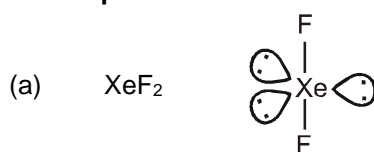
(a) XeF_2

(b) ClO_3^-

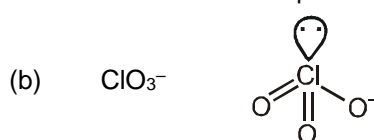
Sol.

Species

Structure



lone pairs occupy the equatorial positions to have minimum repulsion. Thus it is linear.



To minimize the repulsion between lone pair and double bond, species acquires trigonal pyramidal.

Section (B) : Hybridisation

Hybridisation :

- Hypothetical concept Introduced by Pauling and Slater.
- Atomic orbitals of same atom combine to form new set of equivalent orbitals known as hybrid orbitals.
- This phenomenon is known as hybridization.
- Process of intermixing of the atomic orbitals of equal or slightly different energies in the formation of new set of orbitals of equivalent energies and shape is known as hybridization.

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

1. The number of hybrid orbitals is equal to the number of the atomic orbitals that get hybridised.
2. The hybridised orbitals are always equivalent in energy and shape.
3. The hybrid orbitals are more effective in forming stable bonds than the pure atomic orbitals.
4. These hybrid orbitals are directed in space in some preferred direction to have minimum repulsion between electron pairs and thus a stable arrangement is obtained. Therefore, the type of hybridisation indicates the geometry of the molecules.

Important conditions for hybridisation :

- (i) The orbitals present in the valence shell (and sometimes penultimate shell also) of the atom are hybridised.
- (ii) The orbitals undergoing hybridisation should have almost equal energy.
- (iii) Promotion of electron is not essential condition prior to hybridisation.
- (iv) It is the orbital that undergoes hybridization and not the electrons. For example, for orbitals of nitrogen atom ($2s^2 2p_x^1 2p_y^1 2p_z^1$) belonging to valency shell when hybridize to form four hybrid orbitals, one of which has two electrons (as before) and other three have one electron each. It is not necessary that only half-filled orbitals participate in hybridisation. In some cases, even filled orbitals of valence shell take part in hybridisation.

Determination of hybridisation of an atom in a molecule or ion:

Steric number rule (given by Gillespie) :

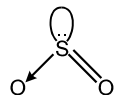
Steric No. of an atom = number of atoms bonded with that atom + number of lone pair(s) left on that atom.

Note : This rule is not applicable to molecules/ions which have odd e^- (ClO_2 , NO , NO_2), free radicals and compounds like B_2H_6 which involve 3-centre $2e^-$ bond (banana bond).

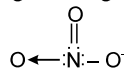
For example :



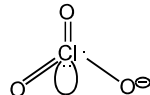
S.No. = 2 + 0 = 2



S.No. = 2 + 1 = 3



S.No. = 3 + 0 = 3



S.No. = 3 + 1 = 4



Table-3

Steric number	Types of Hybridisation	Geometry	Involving orbitals
2	sp	Linear	ns, np _x / p _z / p _y
3	sp ²	Trigonal planar	ns, np _x , p _z / p _y , p _z /p _x , p _y
4	sp ³	Tetrahedral	ns, np _x , p _z , p _y
5	sp ³ d	Trigonal bipyramidal	ns, np _x , p _z , p _y , d _{z²}
6	sp ³ d ²	Octahedral	ns, np _x , p _z , p _y , d _{z²} d _{x²-y²}
7	sp ³ d ³	Pentagonal bipyramidal	ns, np _x , p _z , p _y , d _{z²} d _{x²-y²} , d _{xy}

sp hybridisation :

- This type of hybridisation involves the mixing of one s and one p orbital resulting in the formation of two equivalent sp hybrid orbitals.
- Each sp hybrid orbital has 50% s-character and 50% p-character. Such a molecule in which the central atom is sp-hybridised and linked directly to two other central atoms possesses linear geometry. This type of hybridisation is also known as diagonal hybridisation.
- The two sp hybrids point in the opposite direction along the Z-axis with projecting bigger positive lobes and very small negative lobes, which provides more effective overlapping resulting in the formation of stronger bonds.

Example of a molecule having sp hybridisation

BeCl₂ : The ground state electronic configuration of Be is 1s²2s². In the excited state one of the 2s electrons is promoted to vacant 2p orbital to account for its divalency. One 2s and one 2p-orbitals get hybridised to form two sp hybridised orbitals. These two sp hybrid orbitals are oriented in opposite direction forming an angle of 180°. Each of the sp hybridised orbital overlaps with the 2p-orbital of chlorine axially and form two Be–Cl sigma bonds.

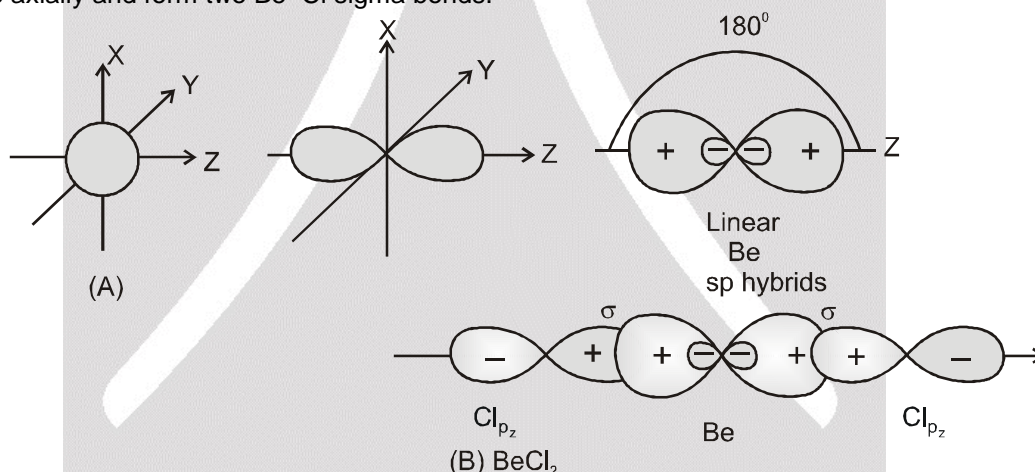


Figure : (A) Formation of sp hybrids from s and p orbitals ; (B) Formation of the linear BeCl₂ molecule.

Examples of sp hybridisation.**Species**

H–C≡N

H–C≡C–H

O=C=O

H₂C=C=CH₂N₃⁻ (azide ion) $\bar{\text{N}} = \overset{+}{\text{N}} = \bar{\text{N}}$ HgCl₂NO₂⁺ (nitronium ion), N₂O

Hydrazoic acid

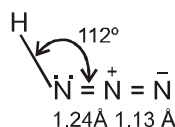
Important characteristic

Linear, highly poisonous, weak acid

Linear, π bond planes are perpendicular

Linear, both π bond are perpendicular to each other

Non planar both hydrogen are perpendicular to each other

Iso electronic with CO₂ and linear in shape. Both N–N bonds are similar



sp² hybridisation :

Mixing of one s and two p orbitals to form 3 equivalent sp² hybridized orbitals.

For example, in BCl₃ molecule, the ground state electronic configuration of central boron atom is 1s² 2s² 2p¹. In the excited state, one of the 2s electrons is promoted to vacant 2p orbital as a result boron has three unpaired electrons.

These three orbitals (one 2s and two 2p) hybridise to form three sp² hybrid orbitals. The three hybrid orbitals so formed are oriented in a trigonal planar arrangement and overlap with 2p orbitals of chlorine to form three B–Cl bonds.

Therefore, in BCl₃, the geometry is trigonal planar with Cl–B–Cl bond angle of 120°.

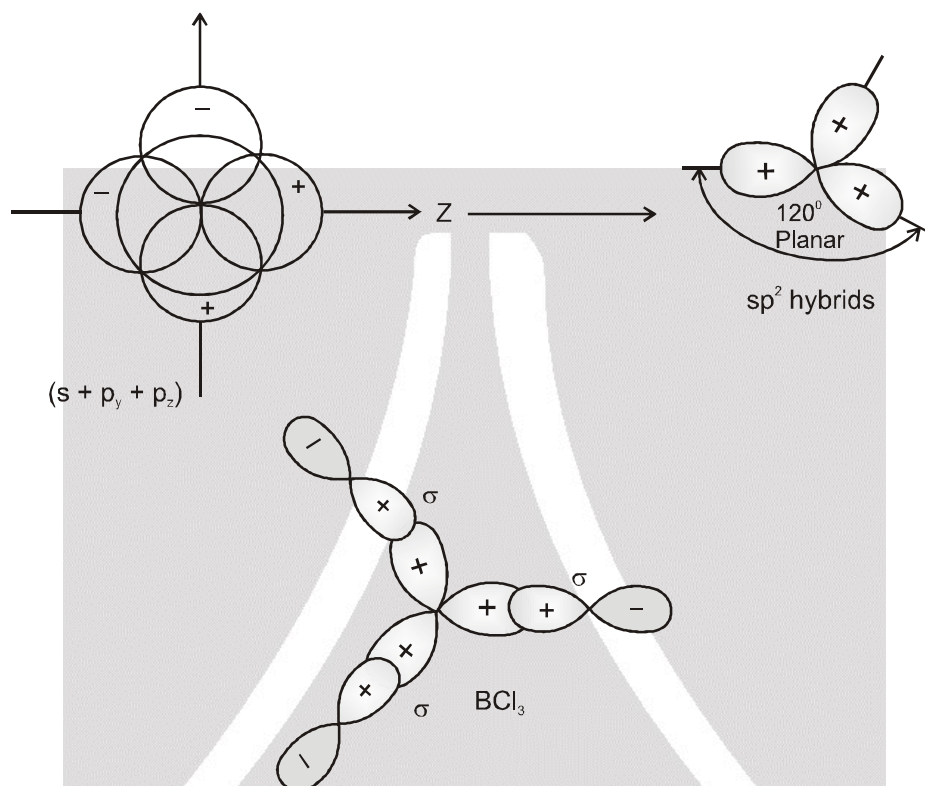


Figure : Formation of sp² hybrids and the BCl₃ molecule

Steric No. = 3

Geometry = Trigonal planar

Ideal bond angle = 120°

Table-4

Type	AB ₃	AB ₂ L
Shape	Trigonal	V-shape (bent)
Example	C ₆ H ₆ , CO ₃ ²⁻ , HCO ₃ ⁻ H ₂ CO ₃ , graphite, BF ₃ B(OH) ₃ , SO ₃ , NO ₃ ⁻ C ₆₀ (Fullerene)	NOCl, O ₃ , NO ₂ , NO ₂ ⁻

Where A = central atom, B = side atom, L = lone pair of e⁻

Molecule	Structure	Statements
SO ₃		All three S–O bonds are equivalent. Out of 3p bond one pπ-pπ other to are pπ-dπ.
O ₃		V shaped molecule. Both O–O bond length are equal.

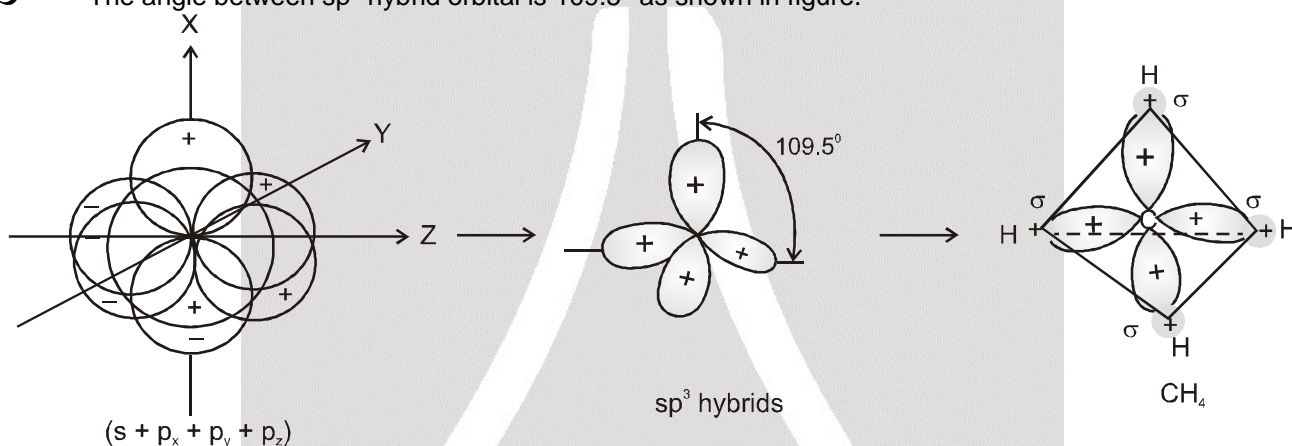


CO_3^{2-}		All three C–O bonds are equivalent. Bond lengths are shorter than single bond length but longer than double bond length.
NO_2^-		Bond order of N–O bond is 1.5, planar molecule.

Note : In N_2O_5 , N is sp^2 hybridised but in solid, N_2O_5 exist in NO_2^+ (N is sp hybridised) and NO_3^- (N is sp^2 hybridised) ions.

sp^3 hybridisation :

- mixing of one s and three p orbitals to form 4 equivalent sp^3 hybridized orbitals.
- 4 sp^3 orbitals are directed towards four corner of tetrahedron.
- This type of hybridisation can be explained by taking the example of CH_4 molecule in which there is mixing of one s-orbital and three p-orbitals of the valence shell to form four sp^3 hybrid orbital of equivalent energies and shape.
- There is 25% s-character and 75% p-character in each sp^3 hybrid orbital. The four sp^3 hybrid orbitals so formed are directed towards the four corners of the tetrahedron.
- The angle between sp^3 hybrid orbital is 109.5° as shown in figure.



Figure

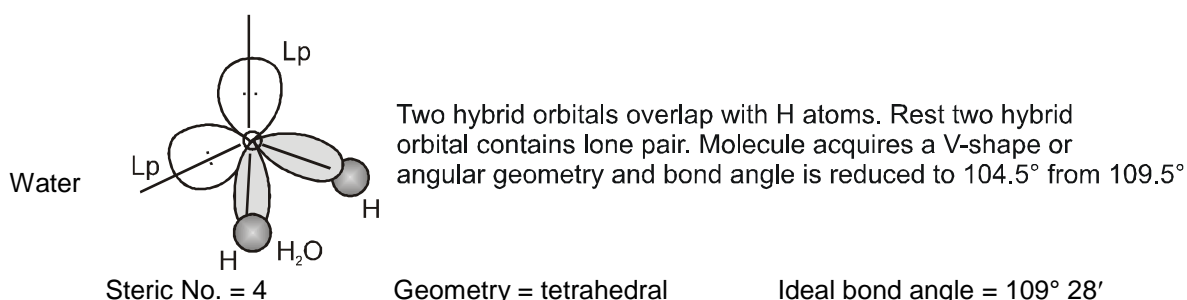
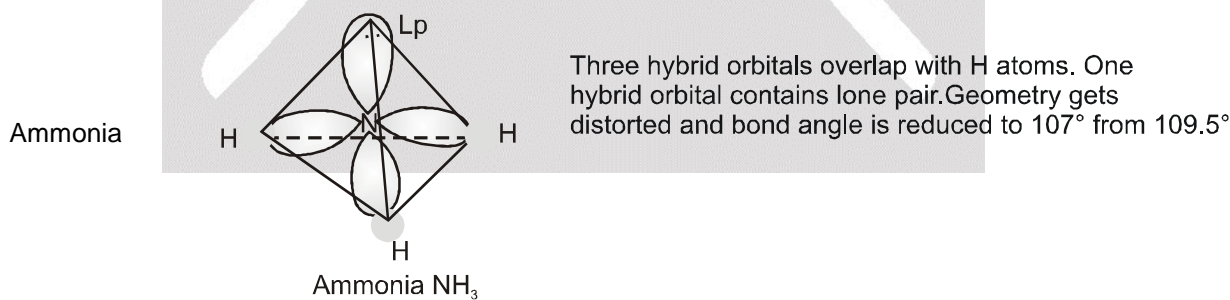
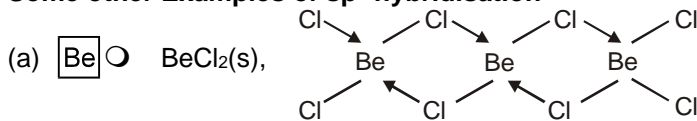


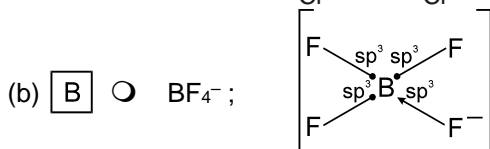


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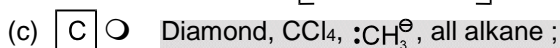
Type	AB ₄	AB ₃ L	AB ₂ L ₂	ABL ₃
Shape	tetrahedral	pyramidal	V-shape or bent	Linear
Example	CH ₄	XeO ₃	OBr ₂	-OCl

Some other Examples of sp³ hybridisation


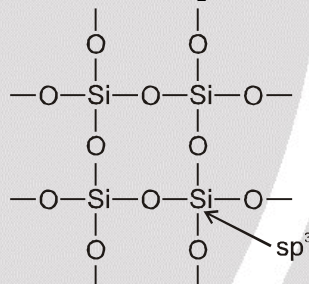
Beryllium chloride in vapour phase contains BeCl₂ and (BeCl₂)_n. In solid state it is in polymeric form.



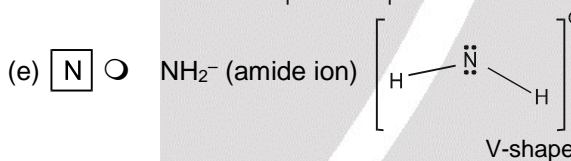
BF₄⁻ ions have a very low tendency to form complexes in aqueous solutions.



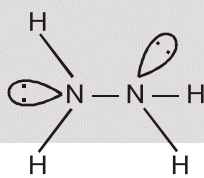
Structure of SiO₂



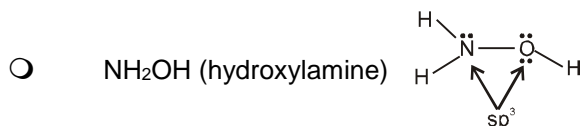
SiO₂ is a covalent network solid like diamond



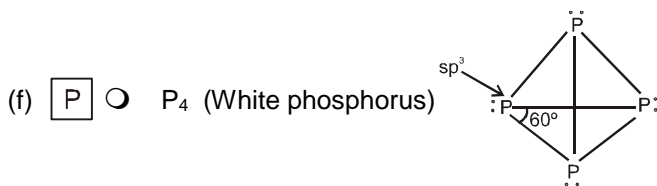
Each N atom is tetrahedrally surrounded by one N, two H and a lone pair.



Structure is similar to that of ethane. The two halves of the molecules are rotated 95° about N-N bond and occupy a gauche (non-eclipsed) conformation. The bond length is 1.45 Å. The bond length is not greater or less than expected bond length of N-N.



lp-lp repulsion increases the N-O bond length.

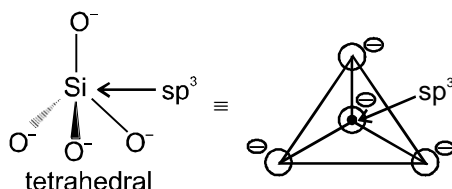


All phosphorus atoms occupy all four vertices of tetrahedron. There are six P-P bonds and \angle P-P-P is 60°.

Since bond angle is 60° (against normal tetrahedral bond angle, 109.5°) so, P₄ molecule is a strained molecule. So it is chemically very reactive.

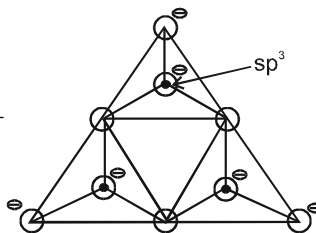


○ Structures of silicate ion : $[\text{SiO}_4]^{4-}$



= Silicon ; O = Oxygen

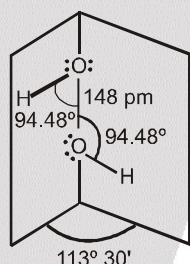
○ Structures of cyclic silicates : $[\text{Si}_3\text{O}_9]^{6-}$



Oxygen atom bonded with two Si atoms can not have negative charge. There is no oxygen-oxygen bond. All silicates contain only Si-O bond and there is no Si-Si Bond.

= Silicon ; O = Oxygen

○ H_2O_2



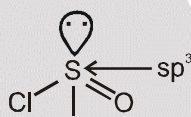
$\text{H}_2\text{O}_2(\text{g})$

O-O bond length (148 pm) is larger than the expected due to the repulsions between the lone pairs on the two oxygen atoms.

It has book like structure (angle between the two pages of the book $113^\circ 30'$).

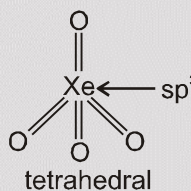
The H_2O_2 is the smallest molecule known to show restricted rotation, in this case about the O-O bond, and this is presumably due to repulsion between the OH groups. A similar structure is retained in the liquid and solid, but bond lengths and angles are slightly changed because of hydrogen bonding.

○ SOCl_2 (Thionyl chloride)



Trigonal pyramidal

○ XeO_4



tetrahedral

● **sp^3d hybridisation :**

Steric number = 5

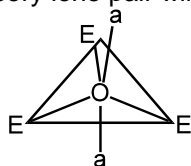
Geometry = trigonal bipyramidal

Table-6

Type	AB_5	AB_4L	AB_3L_2	AB_2L_3
Shape	Trigonal bipyramidal	See-saw	T-shape	Linear
Example	$\text{PCl}_5, \text{PBr}_5, \text{PF}_5$ etc.	$\text{SF}_4, \text{XeO}_2\text{F}_2$	$\text{ClF}_3, [\text{XeF}_3]^+$	$\text{XeF}_2, \text{I}_3^-, [\text{ICl}_2]^-$

Important points regarding sp^3d :

(i) According to VSEPR theory lone pair will occupy equatorial (E) positions but not axial (a).



(ii) More electronegative atoms will prefer to occupy axial positions.

(iii) Since, double bonds occupy more space. Therefore, they will also prefer equatorial positions.



AB₅	PCl ₅ (g)		It is covalent in the gas but in solid state exists as ionic solid consisting of [PCl ₄] ⁺ (tetrahedral) and [PCl ₆] ⁻ (octahedral). All P-Cl bonds are not of equal lengths. Here axial bonds are longer and weaker than equatorial bonds.
	PF ₅ (g)		PF ₅ (g) is trigonal bipyramidal and the electron diffraction shows that some bond angles are 90° and others are 120°, and the axial P-F bond lengths are 1.58 Å while the equatorial P-F lengths are 1.53 Å. But NMR studies suggest that all five atoms are equivalent because of pseudo rotation. PF ₅ remains covalent and is trigonal bipyramidal in the solid state.
	PBr ₅ (g)		PBr ₅ exist as (PBr ₄) ⁺ Br ⁻ in solid state.
	PCl ₃ F ₂		PCl ₃ F ₂ is non polar molecule as all three Cl atoms are at equatorial position and both F atoms in axial position.
	PCl ₂ F ₃		PCl ₂ F ₃ is polar molecule as both Cl atoms and one F atom are at equatorial position and both F atoms in axial position.
AB₄L	SF ₄		SF ₄ molecule have T-shape geometry.
	XeO ₂ F ₂		Both F atoms will be at equatorial position.
AB₃L₂	ClF ₃		T-shape (It is planar molecule)
	I ₃ ⁻		I ₃ ⁻ has linear shape as both I atoms are at axial position.



XeF ₂		XeF ₂ has linear shape as both F atoms are at axial position.
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sp³d² hybridization :

Steric number = 6

Geometry = octahedral

Table-7

Type	AB ₆	AB ₅ L	AB ₄ L ₂
Shape	Octahedral	Square Pyramidal	Square Planar
Example	SF ₆ , PF ₆ ⁻ , [SiF ₆] ²⁻ , [AlF ₆] ³⁻ , [XeO ₆] ⁴⁻	BrF ₅ , IF ₅ , XeOF ₄	ICl ₄ ⁻ , XeF ₄

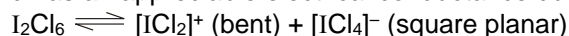
Important : Since, octahedral is a symmetrical figure hence

(a) positions of a lone pair can be any where

(b) but if there are two lone pairs (max.) then these must be in the trans position.

AB₆	SF₆		Bond angle = 90° Due to over-crowding and maximum valency of S, SF ₆ is much less active (almost inert) than SF ₄ .
	[XeO₆]⁴⁻		[XeO ₆] ⁴⁻ is perxenate ion & H ₄ XeO ₆ is called perxenic acid. But H ₂ [XeO ₄] is called xenic acid.
AB₅L	XeOF₄		Molecule has square pyramidal geometry.
AB₄L₂	XeF₄		Molecule has square planar geometry.
	I₂Cl₆		ICl ₃ does not exist, but the dimer I ₂ Cl ₆ is bright yellow solid. Its structure is planar. The terminal I-Cl bonds are normal single bonds of length 2.38 Å and 2.39 Å. The bridging I-Cl bonds appreciably longer (2.68 Å and 2.72 Å) suggesting delocalized bonding rather than simple halogen bridges formed by coordinate bonds from Cl ₂ to I.

Note : The liquid has an appreciable electrical conductance due to self ionization.



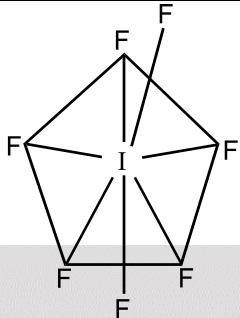
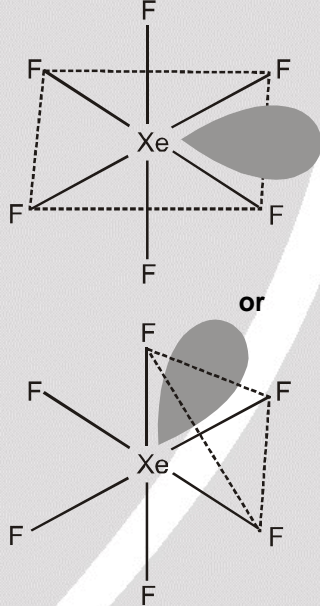
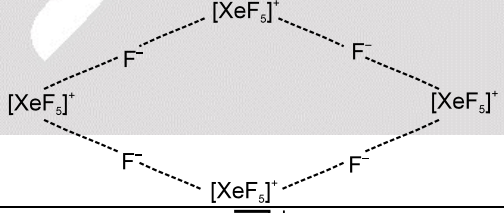
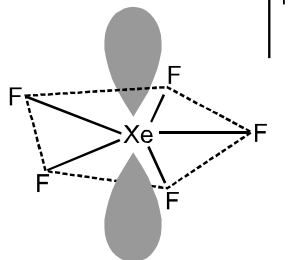
**sp³d³ Hybridization :**

Steric number = 7

Geometry = Pentagonal bi-pyramidal

Table-8

Type	AB ₇	AB ₆ L
Shape	Pentagonal bi-pyramidal	Distorted octahedral
Example	IF ₇	XeF ₆

AB ₇	IF ₇		Bond angle = 72° & 90°
AB ₆ L	XeF ₆ (g)		Distorted octahedron with a nonbonding electron pair either at the centre of a face or the midpoint of an edge.
	XeF ₆ (s)		XeF ₆ (s) is found to be ionic solid consisting of [XeF ₅] ⁺ and F ⁻ ions. It is found that F ⁻ is forming a bridge between two XeF ₅ ⁺ ions.
	[XeF ₅] ⁻		Pentagonal planar ion with two nonbonding electron pairs above and below the plane of the pentagon.



Section (C) : Bond angle, bond length comparison

- (i) Size of atom (see along the group) \propto bond length
 $\text{HF} < \text{HCl} < \text{HBr} < \text{HI}$
 $\text{F-F} < \text{Cl-Cl} < \text{Br-Br} < \text{I-I}$
 $\text{CH}_4 < \text{SiH}_4 < \text{GeH}_4 < \text{SnH}_4$
- (ii) Multiplicity of bond (nearly same period element)
 single bond $>$ double bond $>$ triple bond
 $\text{C-C} > \text{C=C} > \text{C}\equiv\text{C}$
 $\text{F-F} > \text{O=O} > \text{N}\equiv\text{N}$
- (iii) Electronegativity difference (See along the period)
 $\text{H-C} > \text{H-N} > \text{H-O} > \text{H-F}$

HOW TO COMPARE BOND ANGLES

Bond angle depends on the following factor

- I. Hybridisation
- II. No. of lone pair
- III. Size or electronegativity of central atom
- IV. Size or electronegativity of terminal atom

1. Hybridisation :

$$sp > sp^2 > sp^3 > sp^3d^2$$

$$180^\circ \quad 120^\circ \quad 109^\circ 28' \quad 90^\circ$$

2. **Number of lone pair** : If hybridisation of the central atom is same but number of lone pair is different then more is the number of lone pair less is the bond angle.

e.g.	CH_4	NH_3	H_2O
Hybridisation	sp^3	sp^3	sp^3
lone pair	$l.P. = 0$	$l.P. = 1$	$l.P. = 2$
B.A.	$109^\circ 28'$	107°	104°

3. **Size or electronegativity of central atom** : When hybridisation is same and no. of lone pair is same but central atom is different then see the electronegativity of central atom. More is the electronegativity more is the bond angle.

e.g.	NH_3	PH_3	AsH_3	SbH_3
Hybridisation	sp^3	no	no	no
lone pair	$l.P. = 1$	$l.P. = 1$	$l.P. = 1$	$l.P. = 1$
B.A.	107°	93°	92°	91°

4. Size or electronegativity of terminal atom :

Hybridisation same, lone pair same, central atom same but terminal atom is different then greater is the size of the terminal atom greater will be the bond angle. Only in case of fluorine the electronegativity factor is considered, due to greater electronegativity of the fluorine atom the bond angle for it comes out to be smallest (due to smaller bond pair repulsions)

e.g.	PF_3	PCl_3	PBr_3	PI_3
Hybridisation	sp^3	sp^3	sp^3	sp^3
lone pair	$l.P. = 1$	$l.P. = 1$	$l.P. = 1$	$l.P. = 1$
B.A.	98°	100°	101°	102°

Reason : As the E.N. of $x \uparrow$, b.p.-b.p. repulsion will less but l.p. compression will work as usual

Drago rule : Element of 3rd and higher period (4, 5) (p-Block) does not allow hybridisation in molecule when they form bond if they have lone pair on them with less electronegative elements such as hydrogen.

eg : PH_3 , $(\text{CH}_3)_2\text{S}$, AsH_3 , H_2S not have hybridisation.

Bent rule : According to Bent's rule, more electronegative atoms prefer hybrid orbitals having less S character and more electropositive atoms prefer hybrid orbitals having more S character.

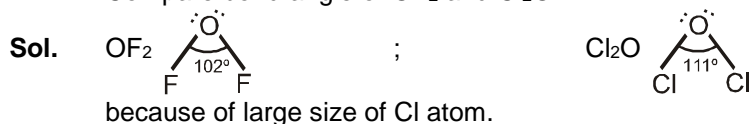
eg : In CH_2F_2 , F-C-F bond angle less than 109.5° indicating less than 25% S character.

H-C-H bond angle more than 109.5° indicating more than 25% S character.

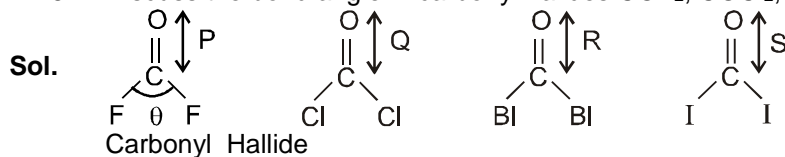


Solved Examples

Ex-2. Compare bond angle of OF_2 and Cl_2O .



Ex-3. Discuss the bond angle in carbonyl halides COF_2 , COCl_2 , COBr_2 , COI_2 .



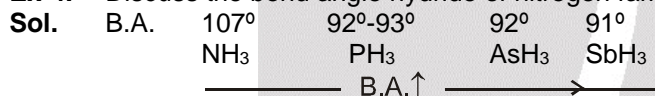
B.A. $\theta \Rightarrow \text{COF}_2 < \text{COCl}_2 < \text{COBr}_2 < \text{COI}_2$

Explanation \Rightarrow

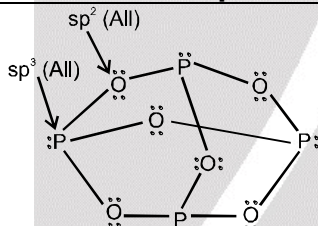
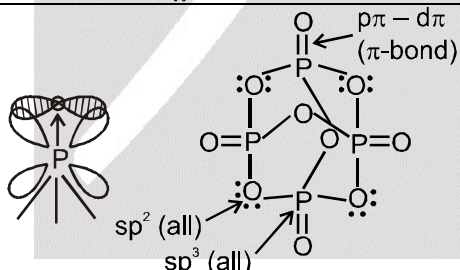
(A) double bonds require more room than single bonds. Hence $\text{C}=\text{O}$ group compresses the molecule and bond angle \downarrow max. in COF_2 . Later on halogen atom becomes bigger and less (-ve) also so \therefore Inter atomic repulsion between the halogens causes \uparrow in B.L.

As X(halogen) becomes less and less (-ve) b.p.-b.p. repulsion also becomes imp and therefore $\theta \uparrow$

Ex-4. Discuss the bond angle hydride of nitrogen family.



Section (D) : Multicentered species

○	P_4O_6		<p>P-O bond length shows that the bridging bonds on the edges are 1.65 \AA and are normal single bonds. There is no P-P bonds.</p>
○	P_4O_{10}		<p>The P-O bond lengths shows that the bridging bonds on the edges are 1.60 \AA but the $\text{P}=\text{O}$ bonds on the corners are 1.43 \AA and this $\text{P}=\text{O}$ is formed by $p\pi-d\pi$ back bonding. A full p-orbital on the oxygen atom overlaps sideways with an empty d-orbital on the phosphorus atom. The bond angle POP is 127° and there is no P-P bonds.</p> <p>Total L.P. = 20. Total no. of p-d bonds = 4</p>