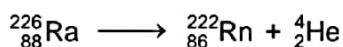


# Group 18

## Occurrence

All the noble gases except radon occur in the atmosphere. Their atmospheric abundance in dry air is ~ 1% by volume of which argon is the major constituent. Helium and sometimes neon are found in minerals of radioactive origin e.g., pitchblende, monazite, cleveite. The main commercial source of helium is natural gas. Xenon and radon are the rarest elements of the group. Radon is obtained as a decay product of  $^{226}\text{Ra}$ .



➤ Most abundant element in air is Ar. Order of abundance in the air is Ar > Ne > Kr > He > Xe.

## ISOLATION

Except He, non-radioactive noble gases are commercially isolated from air by two methods.

### (i) Fractional Distillation of Liquid air (Claude's Method) :

Due to difference in b.p. the various constituents of air are separated from each other.

### (ii) Dewar's Coconut Charcoal Adsorption Method :

- $\text{O}_2$  and  $\text{N}_2$  are removed by means of compound formation.
- The principle of this method is that the adsorption capacity of these gases at low temperature by coconut charcoal increases with increases in their atomic weights.
- Thus He has the lowest and Xe has the maximum adsorption capacity.

### Adsorption of Inert Gases :

- Done on coconut. Gas particles are adsorbed in surface of coconut charcoal
- Larger the size, more will be the adsorption so maximum adsorption of Xe at highest temp.

### Physical properties

All the noble gases are mono-atomic. They are colourless, and tasteless. They are sparingly soluble in water. They have very low melting and boiling points because the only type of interatomic interaction in these elements is weak dispersion forces. Helium has the lowest boiling point (4.2K) of any known substance. It has a unusual property of diffusing through most commonly used laboratory materials such as rubber, glass or plastics.

### Atomic and physical properties

Element	He	Ne	Ar	Kr	Xe
Atomic Number	2	10	18	36	54
Atomic Mass	4	20.18	39.10	83.80	131.30
Electronic configuration	$1s^2$	$[\text{He}] 2s^2 2p^6$	$[\text{Ne}] 3s^2 3p^6$	$[\text{Ar}] 3d^{10} 4s^2 4p^6$	$[\text{Kr}] 4d^{10} 5s^2 5p^6$
Atomic Radius (pm)	120	160	190	200	220
Ionization enthalpy / ( $\text{kJ mol}^{-1}$ )	2372	2080	1520	1351	1170
Density (at STP)/ $\text{g cm}^{-3}$	$1.8 \times 10^{-4}$	$9.0 \times 10^{-4}$	$1.8 \times 10^{-3}$	$3.7 \times 10^{-3}$	$5.9 \times 10^{-3}$
Melting point / K	–	24.6	83.8	115.9	161.3
Boiling point / K	4.2	27.1	87.2	119.7	165.0

**Chemical Properties :** In general, noble gases are least reactive. Their inertness to chemical reactivity is attributed to the following reasons:

- (i) The noble gases except helium ( $1s^2$ ) have completely filled  $ns^2 np^6$  electronic configuration in their valence shell.
- (ii) They have high ionisation enthalpy and more positive electron gain enthalpy.
- The reactivity of noble gases has been investigated occasionally ever since their discovery, but all attempts to force them to react to form the compounds were unsuccessful for quite a few years. In March 1962, Neil Bartlett, then at the University of British Columbia, observed the reaction of a noble gas. First, he prepared a red compound which is formulated as  $O_2^+ PtF_6^-$ . He then realised that the first ionisation enthalpy of molecular oxygen ( $1175 \text{ kJ mol}^{-1}$ ) was almost identical with that of xenon ( $1170 \text{ kJ mol}^{-1}$ ). He made efforts to prepare the same type of compound with  $Xe^+ PtF_6^-$  by mixing  $PtF_6$  and Xenon. After this discovery, a number of xenon compounds mainly with most electronegative elements like fluorine and oxygen, have been synthesised. The compounds of krypton are fewer. Only the difluoride ( $KrF_2$ ) has been studied in detail. Compounds of radon have not been isolated but only identified (e.g.,  $RnF_2$ ) by radiotracer technique. No true compounds of Ar, Ne or He are yet known.

- If Helium is compressed and liquified it forms He(I) liquid at 4.2 K. This liquid is a normal liquid like any other liquid. But if it is further cooled then He(II) is obtained at 2.2 K, which is known as super fluid, because it is a liquid with properties of gases. It climbs through the walls of the container & comes out. It has very high thermal conductivity & very low viscosity.

#### Clathrate compounds :

Inert gas molecules get trapped in the cages formed by the crystal structure of water.

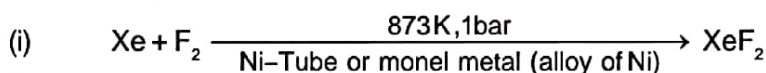
During the formation of ice Xe atoms will be trapped in the cavities (or cages) formed by the water molecules in the crystal structure of ice. Compounds thus obtained are called clathrate compounds.

There are no chemical bonds. They do not possess an exact chemical formula but approx it is 6 water molecules: 1 inert gas molecule. The cavity size is just smaller than the atom of the noble gas. Such compounds are also formed by the other organic liquids like dihydroxybenzene (for example quinol). The smaller noble gases He and Ne do not form clathrate compounds because the gas atoms are small enough to escape from the cavities. Clathrate provides a convenient means of storing radioactive isotopes of Kr and Xe produced in nuclear reactors.

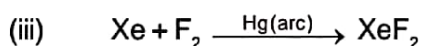
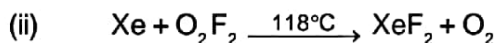
#### COMPOUNDS OF XENON :

##### XENON DIFLUORIDE ( $XeF_2$ ):

##### Preparation:

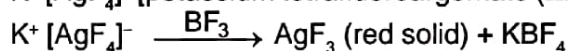


- Volume ratio should be 2 : 1 otherwise other higher fluorides tend to form.



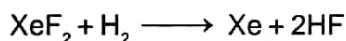
- (iv) Recently discovered method :

$K^+ [AgF_4]^-$  [potassium tetrafluoroargentate (III)] is first prepared and this is reacted with  $BF_3$ .

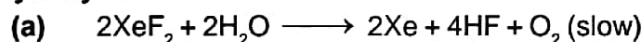


##### Properties :

- (i) Colorless crystalline solid and sublimates at 298 K.
- (ii) Dissolves in water to give a solution with a pungent odour. Much soluble in HF liquid.
- (iii) This is stored in a vessel made up of monel metal which is an alloy of nickel.
- (iv) **Reaction with  $H_2$  :** It reacts with hydrogen gas at  $400^\circ C$

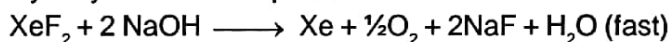


- (v) **Hydrolysis :**



The above is neither a cationic hydrolysis nor an anionic hydrolysis as seen in ionic equilibrium. It is a covalent compound and hydrolysis is like that of  $PCl_5$ .

(b) Hydrolysis is more rapid with alkali.

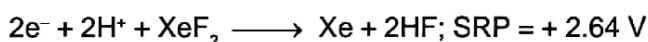


The reaction (a) is slower probably due to dissolution of  $XeF_2$  in HF.

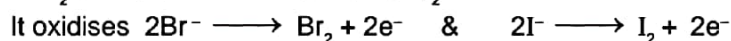
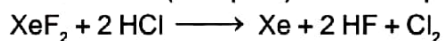
- (vi) **Oxidising properties :**

Higher the value of SRP better is the oxidising property of the species.

The standard reduction potential for  $XeF_2$  is measured to be + 2.64 V. Therefore, it acts as a strong oxidising agent.

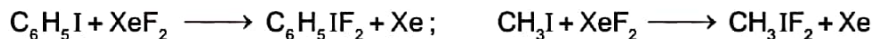


This oxidises halides (except F<sup>-</sup>) to their respective halogens.



➤ Similarly it can oxidise BrO<sub>3</sub><sup>-</sup> (bromate) which are themselves good oxidising agents to BrO<sub>4</sub><sup>-</sup> (perbromate ions) and Ce<sup>3+</sup> to Ce<sup>4+</sup> ion.

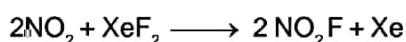
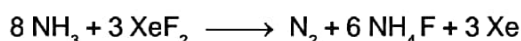
(vii) **Oxidising as well as fluorinating properties** : It can act as strong oxidising agent as well as fluorinating agent.



➤ CH<sub>3</sub>IF<sub>2</sub> exists as CH<sub>3</sub><sup>+</sup>IF<sub>2</sub><sup>-</sup>, IF<sub>2</sub><sup>-</sup> is analogous to I<sub>3</sub><sup>-</sup>

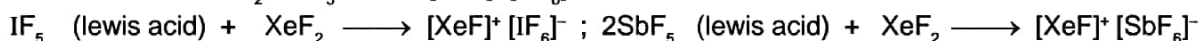
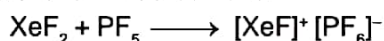
➤ F<sub>3</sub><sup>-</sup> can not be formed as it has no d-orbitals to attain sp<sup>3</sup>d hybridisation.

(viii) **Reactions of XeF<sub>2</sub> + HF (anhydrous)** :



(nitronium fluoride)

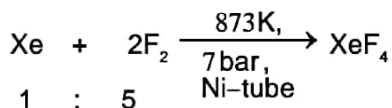
(ix) **Formation of addition compounds** : XeF<sub>2</sub> reacts with fluoride ion acceptors to form cationic species and fluoride ion donors to form fluoroanions.



➤ Similar behaviour is shown by PF<sub>5</sub> and AsF<sub>5</sub>

### **XENON TETRAFLUORIDE (XeF<sub>4</sub>) :**

**Preparation :**



**Properties :**

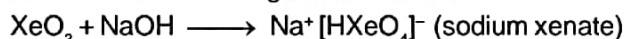
(i) It is a colorless crystalline solid and sublimes at 298 K.

(ii) It undergoes sublimation, soluble in CF<sub>3</sub>COOH. It undergoes hydrolysis violently hence no moisture must be present during its preparation.

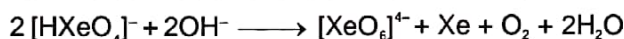
(iii) **Reaction with H<sub>2</sub>O** :  $6 \text{XeF}_4 + 12 \text{H}_2\text{O} \longrightarrow 4 \text{Xe} + 2\text{XeO}_3 + 24 \text{HF} + 3\text{O}_2$

➤ XeO<sub>3</sub> is white solid and explosive compound (dry), soluble in water (well behaved in water)

➤ XeO<sub>3</sub> reacts with NaOH forming sodium xenate

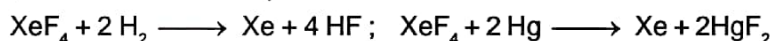


➤ It disproportionates into perxenate ion in basic medium.



Xenic acid (H<sub>2</sub>XeO<sub>4</sub>) is a very weak acid.

(iv) **Oxidising properties of XeF<sub>4</sub> :**



(v) **Addition reactions** : XeF<sub>4</sub> reacts with fluoride ion acceptors to form cationic species and fluoride ion donors to form fluoroanions.



### **XENON HEXAFLUORIDE (XeF<sub>6</sub>) :**

**Preparation:**

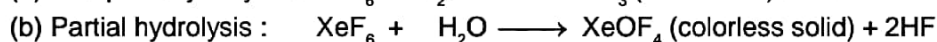
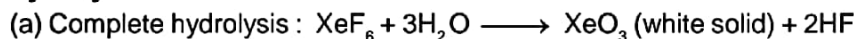




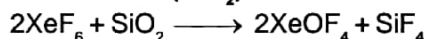
### Properties:

- (i) Colourless crystalline solid and sublimes at 298 K.
- (ii) It gives yellow liquid on melting where as other form white liquids on melting (a point of difference)
- (iii) HF is a good solvent for all three fluorides.

### (iv) Hydrolysis :



### (v) Reaction with silica ( $\text{SiO}_2$ ) :

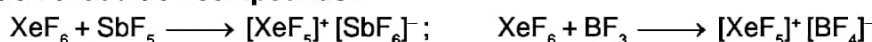


### (vi) Thermal decomposition (effect of heat) :



➤  $\text{XeF}_2$  &  $\text{XeF}_4$  do not undergo decomposition

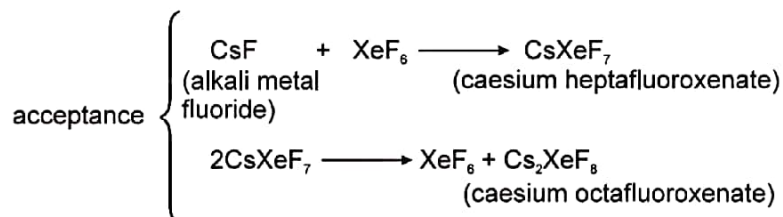
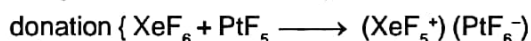
### (vii) Formation of addition compounds :



### (viii) Reaction With $\text{H}_2$ : $\text{XeF}_6 + 3\text{H}_2 \longrightarrow 6\text{HF} + \text{Xe}$

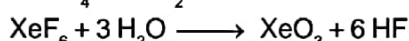
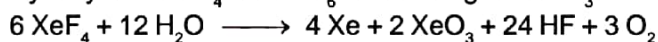
### (ix) Reaction of $\text{XeF}_6$ with $\text{XeO}_3$ : $\text{XeO}_3 + 2\text{XeF}_6 \longrightarrow 3\text{XeOF}_4$

### (x) F<sup>-</sup> donating/ F<sup>-</sup> accepting properties : $\text{XeF}_6$ reacts with fluoride ion acceptors to form cationic species and fluoride ion donors to form fluoroanions.

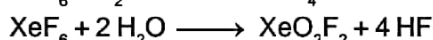
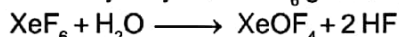


### XENON-OXYGEN COMPOUNDS :

Hydrolysis of  $\text{XeF}_4$  and  $\text{XeF}_6$  with water gives  $\text{XeO}_3$ .



Partial hydrolysis of  $\text{XeF}_6$  gives oxyfluorides,  $\text{XeOF}_4$  and  $\text{XeO}_2\text{F}_2$ .



$\text{XeO}_3$  is a colourless explosive solid and has a pyramidal molecular structure.  $\text{XeOF}_4$  is a colourless volatile liquid and has a square pyramidal molecular structure.

### Uses :

Helium is a non-inflammable and light gas. Hence, it is used in filling balloons for meteorological observations. It is also used in gas-cooled nuclear reactors. Liquid helium (b.p.4.2 K) finds use as cryogenic agent for carrying out various experiments at low temperatures. It is used to produce and sustain powerful superconducting magnets which form an essential part of modern NMR spectrometers and Magnetic Resonance Imaging (MRI) systems for clinical diagnosis. It is used as a diluent for oxygen in modern diving apparatus because of its very low solubility in blood.

Neon is used in discharge tubes and fluorescent bulbs for advertisement display purposes. Neon bulbs are used in botanical gardens and in green houses.

Argon is used mainly to provide an inert atmosphere in high temperature metallurgical process (arc welding of metals or alloys) and for filling electric bulbs. It is also used in the laboratory for handling substances that are air-sensitive.

Xenon and Krypton are used in light bulbs designed for special purposes.

**Q. 57. Give a brief VSEPR explanation of structures of Xenon fluorine compounds.**

**Ans.** The structure of xenon and fluorine compounds can be summarised as follows :

Compound	Structure	No. of electron pairs	No. of lone pairs	VSEPR explanations
XeF <sub>2</sub>	Linear	5	3	5 electron pairs form trigonal bipyramid with three lone pairs at equatorial positions.
XeF <sub>4</sub>	Square planar	6	2	6 electron pairs form an octahedron with two position occupied by lone pairs.
XeF <sub>6</sub>	Distorted octahedron	7	1	Pentagonal bipyramid with one lone pair.
XeO <sub>3</sub>	Pyramidal	7	1	Three $\pi$ bonds so the remaining 4 electron pairs form a tetrahedron with one lone pair.
XeO <sub>2</sub> F <sub>2</sub>	Trigonal bipyramid	7	1	Two $\pi$ bonds so the remaining 5 electron pairs form trigonal bipyramid with one lone pair at equatorial position.
XeOF <sub>4</sub>	Square pyramidal	7	1	One $\pi$ bond so the remaining 6 electron pairs form an octahedron with one position occupied by lone pair.
XeO <sub>4</sub>	Tetrahedral (T <sub>d</sub> )	8	0	Four $\pi$ bonds so remaining four electron pairs form a tetrahedron.
XeO <sub>3</sub> F <sub>2</sub>	Trigonal bipyramidal (D <sub>3h</sub> )	8	0	Three $\pi$ bonds so remaining five electron pairs form a trigonal bipyramid.
[XeO <sub>6</sub> ] <sup>4-</sup>	Octahedral (O <sub>h</sub> )	8	0	Two $\pi$ bonds so the remaining 6 electron pairs form an octahedron.

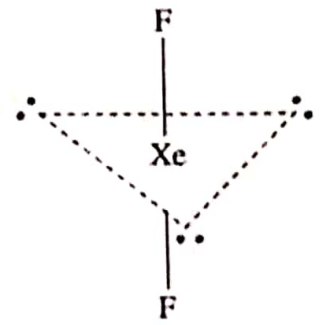
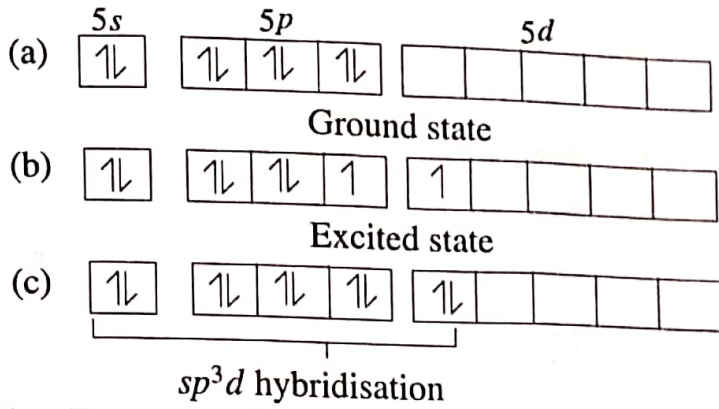
**Q. 58. Draw the structures of following compounds :**

(i) XeF<sub>2</sub> (ii) XeF<sub>4</sub> (iii) XeF<sub>6</sub> (iv) XeO<sub>3</sub> (v) XeOF<sub>4</sub> (vi) XeO<sub>2</sub>F<sub>2</sub> (vii) XeO<sub>4</sub> (viii) [XeO<sub>6</sub>]<sup>4-</sup>

**Ans.** XeF<sub>2</sub>—There are 10 valence electrons (8 from valence shell of xenon 5s<sup>2</sup> 5p<sup>6</sup> and two from the two bonded fluorine atoms) to be filled in orbitals. These require **five orbitals** which can be formed by the hybridisation of one 5s, three 5p and one 5d orbitals (sp<sup>3</sup>d hybridization). These are directed towards the five corners of a trigonal bipyramid. Two of these contain shared electrons, the other three lone pairs. For greatest stability, the shared pairs are as far apart as possible, so Xe – F bonds are at 180° to each other and the structure is **linear**.



**Xenon atom**



**Fig. : Formation of  $XeF_2$  molecule by  $sp^3d$  hybridisation. Electrons supplied by fluorine atoms are represented by dotted arrows.**

**$XeF_4$** —In a similar manner we have  $8 + 4$  or  $12$  valence electrons to accommodate ( $8$  being electrons of the central atom and  $4$  being electrons from  $4$  fluorine atoms). These require  $6$  orbitals, hence  $sp^3d^2$  hybridization. The structure is square planar and the four fluorine atoms are in the same plane alongwith Xenon atom. The six orbitals are directed towards the six corners of an octahedron. The two lone pairs are one above one below the plane containing Xe and  $4$  fluorine atoms.

Formula of compound	Type of hybridisation	No. of bond pairs of electrons	No. of lone pairs of electrons	Type of arrangement of electron pairs	Geometry of molecule	Bond angle	Structure of molecule
$XeF_2$ ( $D_{\infty H}$ )	$sp^3d$	2	3	Trigonal bipyramidal	Linear ( $D_{\infty H}$ )	$180^\circ$	
$XeF_4$ ( $D_{4h}$ )	$sp^3d^2$	4	2	Octahedral	Square planar	$90^\circ$	
$XeF_6$ ( $C_{3v}$ )	$sp^3d^3$	6	1	Pentagonal bipyramidal	Distorted octahedral	$\approx 90^\circ$	
$XeOF_2$ ( $C_{2v}$ )	$sp^3d$	$3\sigma$ $1\pi$	2	Trigonal bipyramidal	T-shaped	—	

$\text{XeOF}_4$ ( $C_{4v}$ )	$sp^3d^2$	$5\sigma$ $1\pi$	1	Octahedral	Square pyramidal	—	
$\text{XeO}_2\text{F}_2$ ( $C_{2v}$ )	$sp^3d$	$4\sigma$ $2\pi$	1	Trigonal bipyramidal	Distorted trigonal bipyramidal	—	
$\text{XeO}_3$ ( $C_{3v}$ )	$sp^3$	$3\sigma$ $3\pi$	1	Tetrahedral	Pyramidal	—	
$\text{XeO}_2\text{F}_4$	$sp^3d^2$	$6\sigma$ $2\pi$	—	Octahedral	Octahedral	$90^\circ$	
$\text{XeO}_3\text{F}_2$ ( $D_{3h}$ )	$sp^3d$	$5\sigma$ $3\pi$	—	Trigonal bipyramidal	Trigonal bipyramidal	—	
$\text{XeO}_4$ ( $T_d$ )	$sp^3$	$4\sigma$ $34\pi$	—	Tetrahedral	Tetrahedral	—	

## Xenon Atom

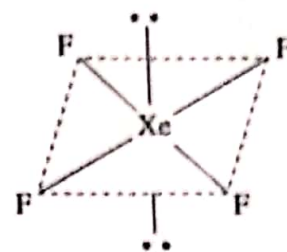
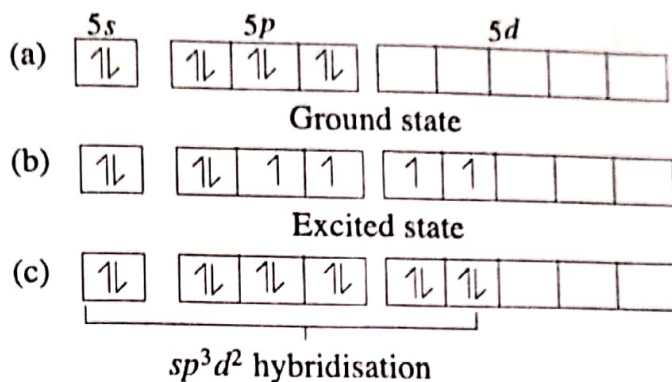
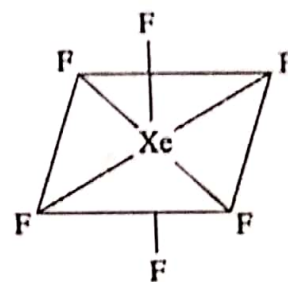
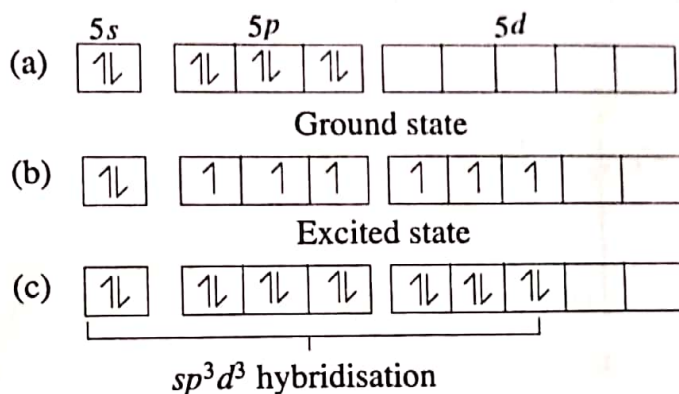


Fig. : Formation of  $XeF_4$  molecule by  $sp^3d^2$  hybridisation.

$XeF_6$ —Here, we have  $8 + 6$  or  $14$  electrons to accommodate. These need  $7$  orbitals. Hence,  $sp^3d^3$  hybridisation resulting in distorted octahedron.

## Xenon Atom



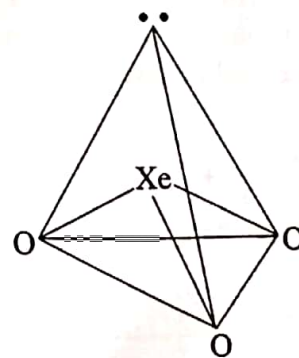
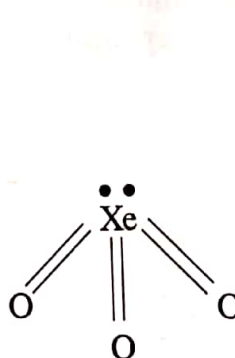
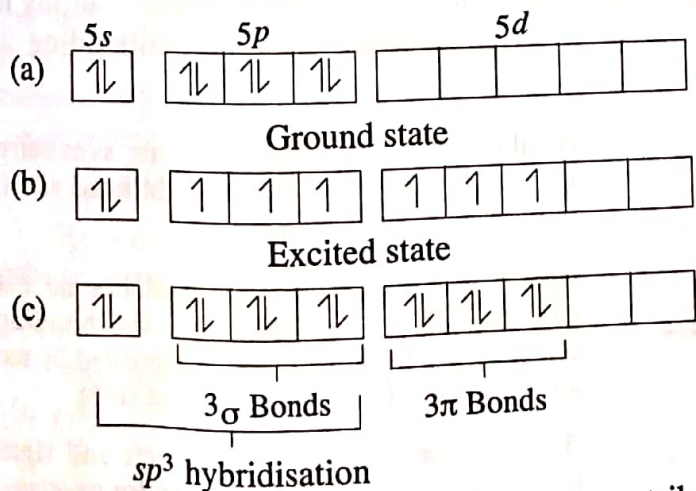
Slightly distorted octahedron Xenon hexafluoride  $XeF_6$ .

Fig. : Formation of  $XeF_6$  molecule by  $sp^3d^3$  hybridisation.

The shapes of oxygen containing compounds of Xe are correctly predicted by the valence bond method. (Electrons in  $\pi$  bonds (double bonds) must be subtracted before counting the number of electron pairs which determine the primary shape of the molecule.

$XeO_3$ —Oxygen shares three of the four lone pairs of xenon. Hence, only  $8$  valence electrons are to be accommodated and hybridisation around xenon is  $sp^3$ . As three orbitals contain bond pairs and one lone pair, so the geometry is described as trigonal pyramid. The  $O-Xe-O$  bond angle is found to be  $103^\circ$  and is reasonably close to the expected  $\approx 109^\circ$ , taking into account the greater repulsion between lone pair and bond pairs as compared to bond pair-bond pair repulsion.

## Xenon Atom

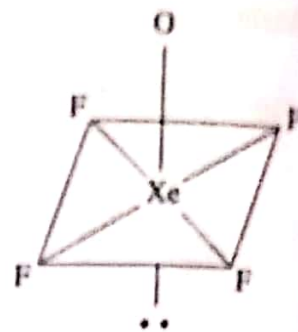
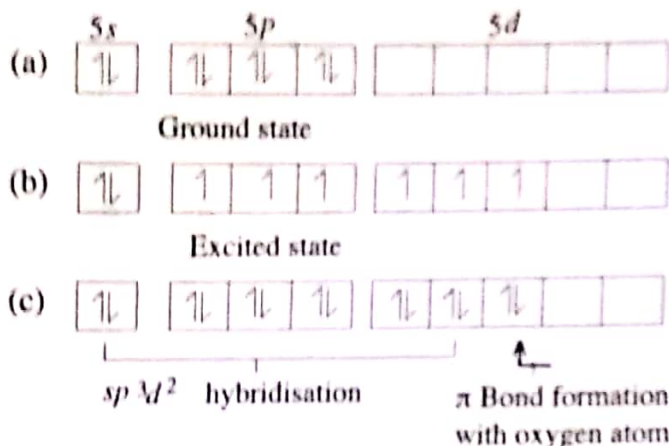


Pyramidal Xenon trioxide  $XeO_3$ .

$XeOF_4$ —Here, oxygen atom does not contribute any electrons but shares one of the lone pairs of xenon. Hence, the structure is like that of  $XeF_4$  in which one of the orbitals containing lone pairs

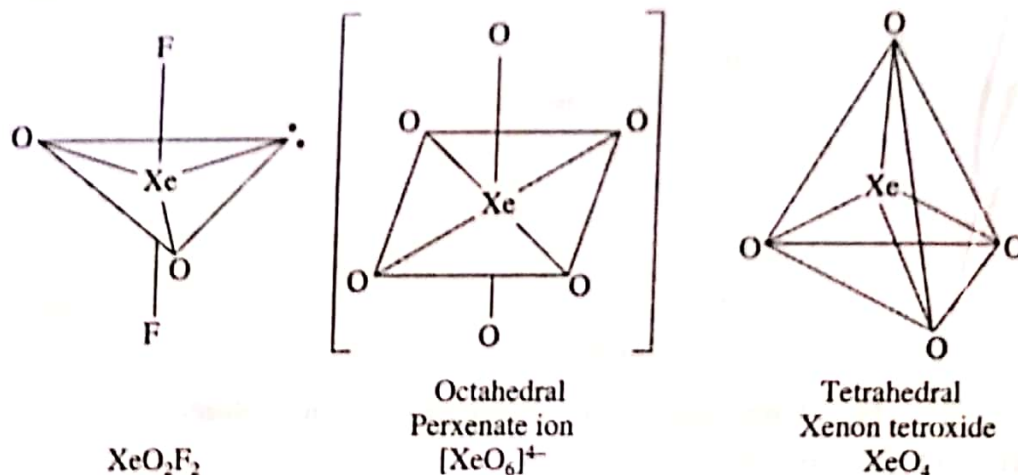


**Xenon Atom**



Square pyramidal (octahedral with one position unoccupied) Xenon oxyfluoride  $XeOF_4$ .

around xenon is replaced by  $Xe-O$  bond. The structure is described as square pyramid. The six orbitals, as before, are arranged towards the six corners of a regular octahedron. The structure of  $XeO_2F_2$ ,  $[XeO_6]^{4-}$  and  $XeO_4$  can be described on similar lines. The structures are shown below:

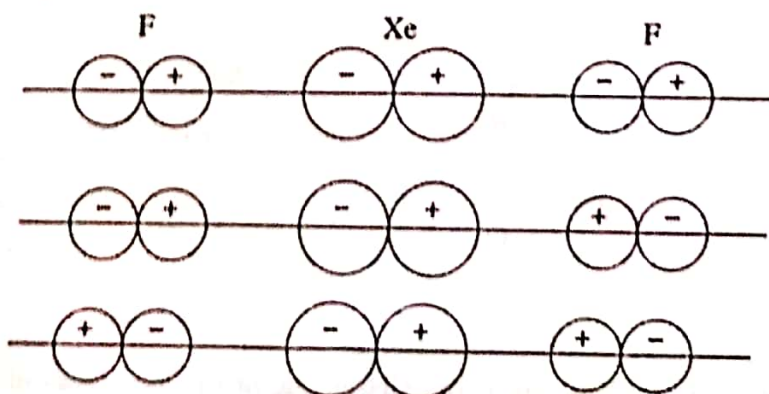


**Q. 59. Explain the structure of  $XeF_2$  on the basis of molecular orbital theory.**

**Ans.** The outer electronic configuration of xenon and fluorine atoms are



Assume that bonding involves the  $5p_z$  orbital of Xe and  $2p_z$  orbitals of two F atoms. For bonding to occur, orbitals with the same symmetry must overlap. These three atomic orbitals combine resulting in the formation of three molecular orbitals, one bonding, one non-bonding and one antibonding as represented below—



Antibonding (orbitals have wrong symmetry for overlap on both left and right hand sides, indicated by + and - signs).

Non-bonding (the Xe  $5p$  orbital has no net contribution to bonding, since the bonding effect on the right hand side is cancelled by the antibonding effect on the left hand side).

Bonding (orbitals on both the left and right hand sides have correct symmetry for overlap).

Fig. • Possible combinations of atomic orbitals in  $XeF_2$

The original three atomic orbitals contain four electrons (two in the Xe  $5p_z$  and one in each of the F  $2p_z$ ). These occupy the molecular orbitals of the lowest energy. Two of these occupy bonding MO and two occupy non-bonding MO, their energies being in the order—  
 Bonding MO < non-bonding MO < antibonding MO.  
 The bonding may be described as three centre, four electrons  $\sigma$ -bonding. A linear combination of the atoms gives the best overlap of the orbitals.

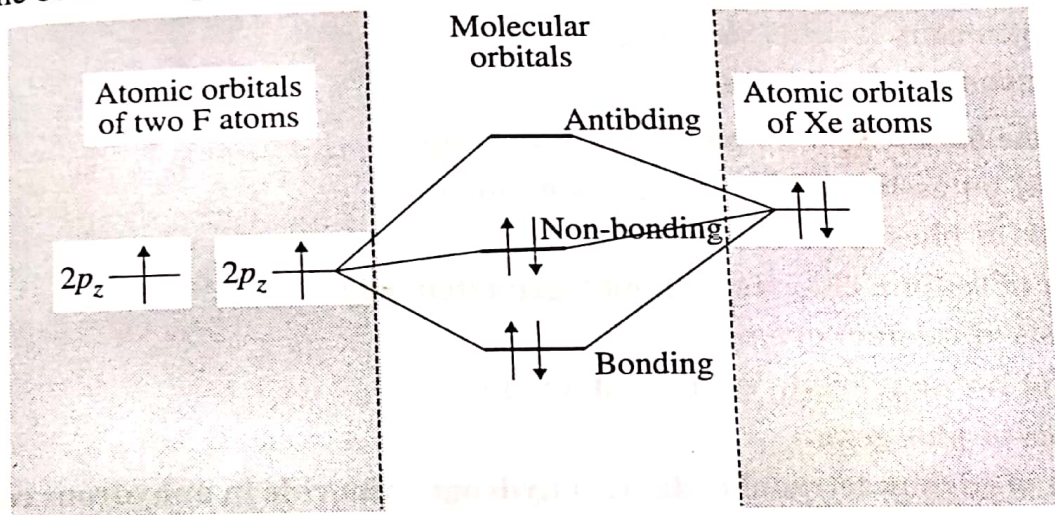


Fig. : Molecular orbitals in  $\text{XeF}_2$ .

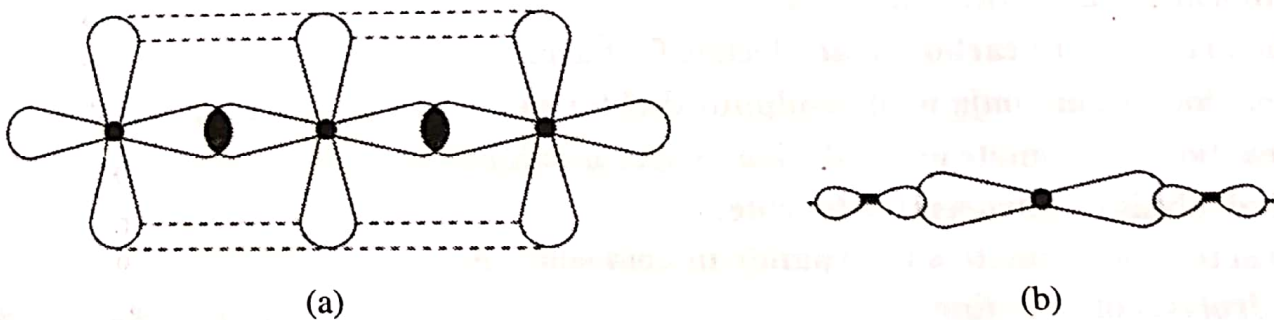


Fig. : Linear combination of  $p_z$  orbitals of xenon and fluorine in  $\text{XeF}_2$ .