This notes / material is as per the prescribed syllabus of Banaras Hindu University for the 2nd sem. B.Sc. (H) course, Paper: CHB-201 (A).

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Noble Gases

Syllabus: Structures of Xe compounds: XeF_2, XeF_4, XeF_6, XeO_3, XeO_2F_2, $XeOF_4$, XeO_4, XeO_3F_2 and $[XeO_6]^{4-}$

Helium (He), Neon (Ne), Argon (Ar), Krypton (Kr), Xenon (Xe) and Radon (Rn) are the elements of Group 18, also known as noble gases. Except Radon, all the gases are present in the atmosphere, while Rn is obtained by disintegration of radium and is itself radioactive.

With a filled valence shell electronic configuration (ns^2np^6), these elements have very little tendency to form compounds and were hence called ***inert gases***. Their inactivity is further accepted due to their high ionisation energies and almost zero electron affinities.

However, observation by *Bartlett in 1962*, of the formation of an orange yellow solid even at room temperature, upon mixing deep red vapors of PtF_6 with excess of Xe vapors (identified as $Xe^+PtF_6^-$), changed the notion that these gases are inert and are called **noble gases**.

A look at the ionisation energies (in kJ/mol) of these elements reveals that the ionisation energies of Kr and Xe are comparable to that of C, N and O. Therefore, Xe forms largest number of compounds followed by Kr. Since, the reactivity of Xe and Kr, arises out of their tendency to lose electrons, the combining element must have very highly electronegativity. For this reason, Xe and Kr mostly forms compounds with F and O, known as fluorides, oxides and oxyfluorides.

Element	I.E. (kJ/mol)
He	2372.1
Ne	2080.4
Ar	1520.3
Kr	1350.6
Xe	1170.2
C	1086
N	1402
O	1313.7

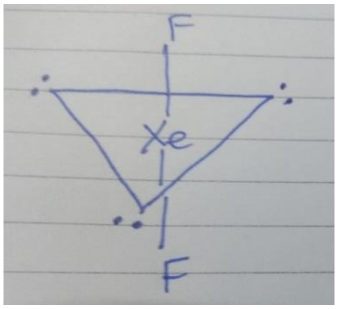
Xe forms a number of fluorides, oxides and oxyfluorides in its different oxidation states.

Xe(II) compounds

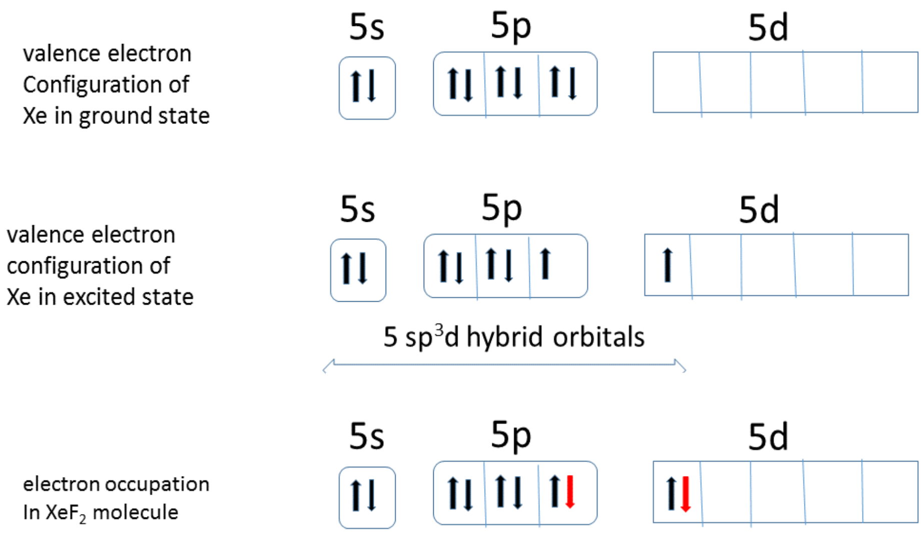
Xenon difluoride (XeF_2): Heating xenon and fluorine in 2:1 molar ratios in a sealed nickel tube at 400 °C, yields XeF_2 as a colorless solid upon cooling.

$$Xe + F_2 \longrightarrow XeF_2$$

XeF_2 has a linear structure as revealed by spectroscopic analysis, which may be explained based on VSEPR theory.



In its ground state, Xe has $5s^2 5p^6$ configuration. In the excited state, one of the 5p electron gets excited to 5d level, leaving 3 filled (one 5s and two 5p) orbitals and two half filled orbitals (one 5p and one 5d). All the filled and partially filled orbitals hybridise to give 5 **sp^3d** orbitals. Two hybrid orbitals having unpaired electrons overlap with the half filled 2p orbitals of fluorine, to form two Xe-F bonds. The two Xe-F bonds lie in a straight line, while the orbitals having lone pairs lie at the corners of the equatorial plane, to minimise repulsions. Thus, the molecule (XeF_2) has a ***linear shape***.



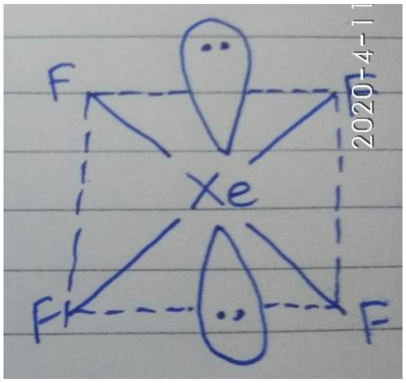
Hybridisation scheme for XeF_2

Xe(IV) compounds

(a) ***Xenon tetrafluoride (XeF_4):*** Passing mixture of Xe and F_2 in 1:5 molar ratios through a nickel tube at 400 ºC under a pressure of 5-6 atm. Yields XeF_4.

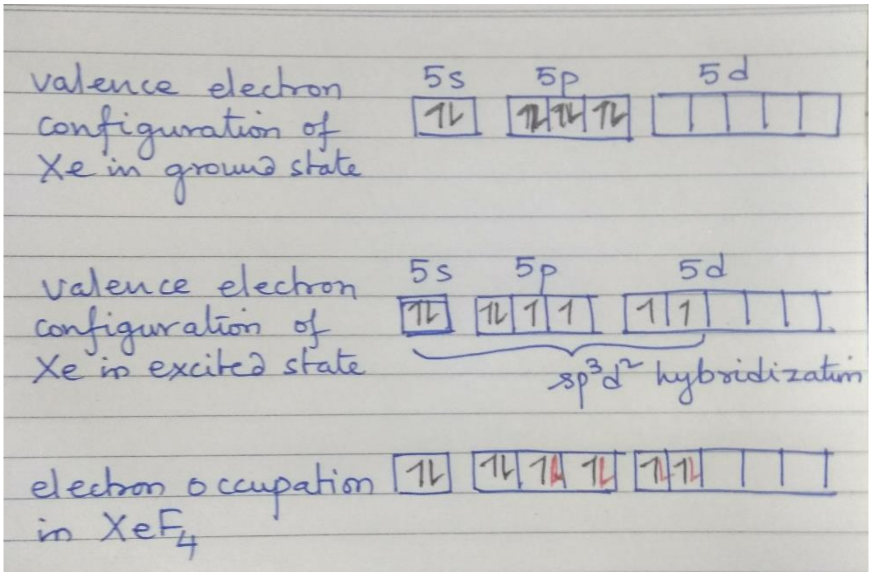
$$Xe + 2F_2 \rightarrow XeF_4$$

XeF_4 has a square planar shape, with the F atoms at the corners of the square plane and two lone pairs at the axial positions, to minimise repulsions. The structure may be explained based on VSEPR theory as below.



In the formation of XeF_4 molecule, two of the 5p electrons, go into the 5d orbital. Hence, in the excited state, Xe has four unpaired electrons (two in 5p and two in 5d) and two lone pair electrons (one 5s and one 5p). All the six orbitals hybridise to give six **sp^3d^2** hybrid orbitals. Among the six orbitals, four orbitals having unpaired electrons, overlap with the orbitals of fluorine having unpaired electrons and form

4 Xe-F bonds, which are directed at the corners of the square plane. Two orbitals having lone pair electrons are opposite to each other, oriented towards the axial positions of the octahedron. Hence, the molecule has a ***square planar shape***.

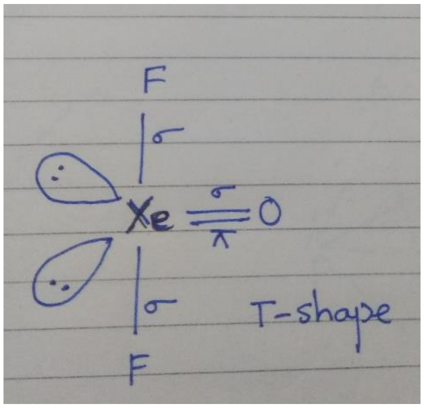


Hybridisation scheme for XeF_4.

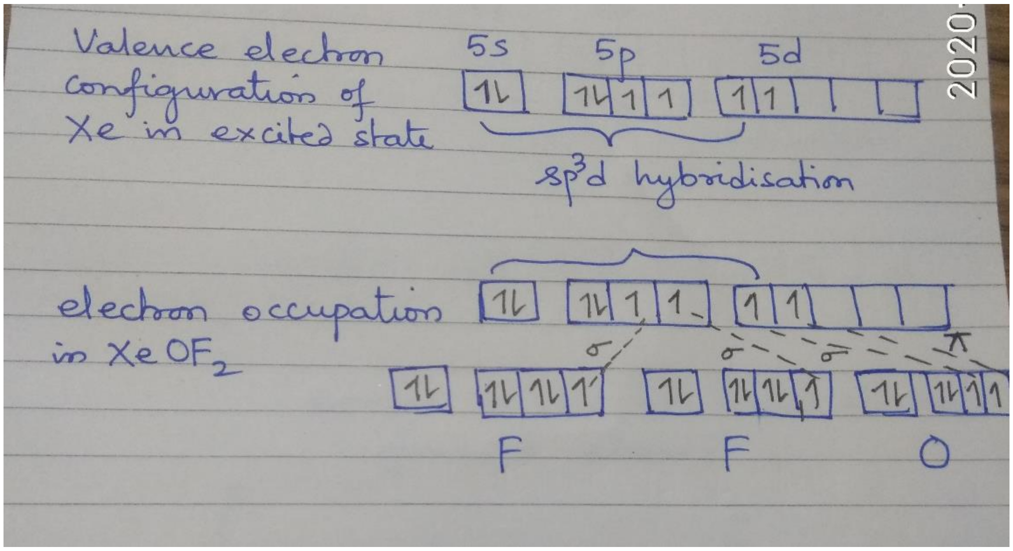
(b) ***Xenon Oxodifluoride ($XeOF_2$):*** Slow and partial hydrolysis of XeF_4 at low temperatures (-80 ºC), yields, not very stable $XeOF_2$.

$$XeF_4 + H_2O \rightarrow XeOF_2 + 2HF$$

The structure of the molecule is of T-shape, with the O atom and two lone pairs in the trigonal plane and two of the F atoms occupying the axial positions of the trigonal pyramid.



Such a structure may be explained on the basis of **sp^{3}d** hybridisation of Xe valence orbitals, due to which Xe will have two lone pairs and three unpaired electrons in the hybrid orbitals. The unpaired electrons form bonds with the unpaired electrons of one oxygen and two fluorinw atoms. The unpaired electron of Xe, which is not taking part in hybridisation, overlaps sideways with the other unpaired electron of the same oxygen atom forming a double bond. Hence, the final shape of the molecule will be of ***T-shape***.



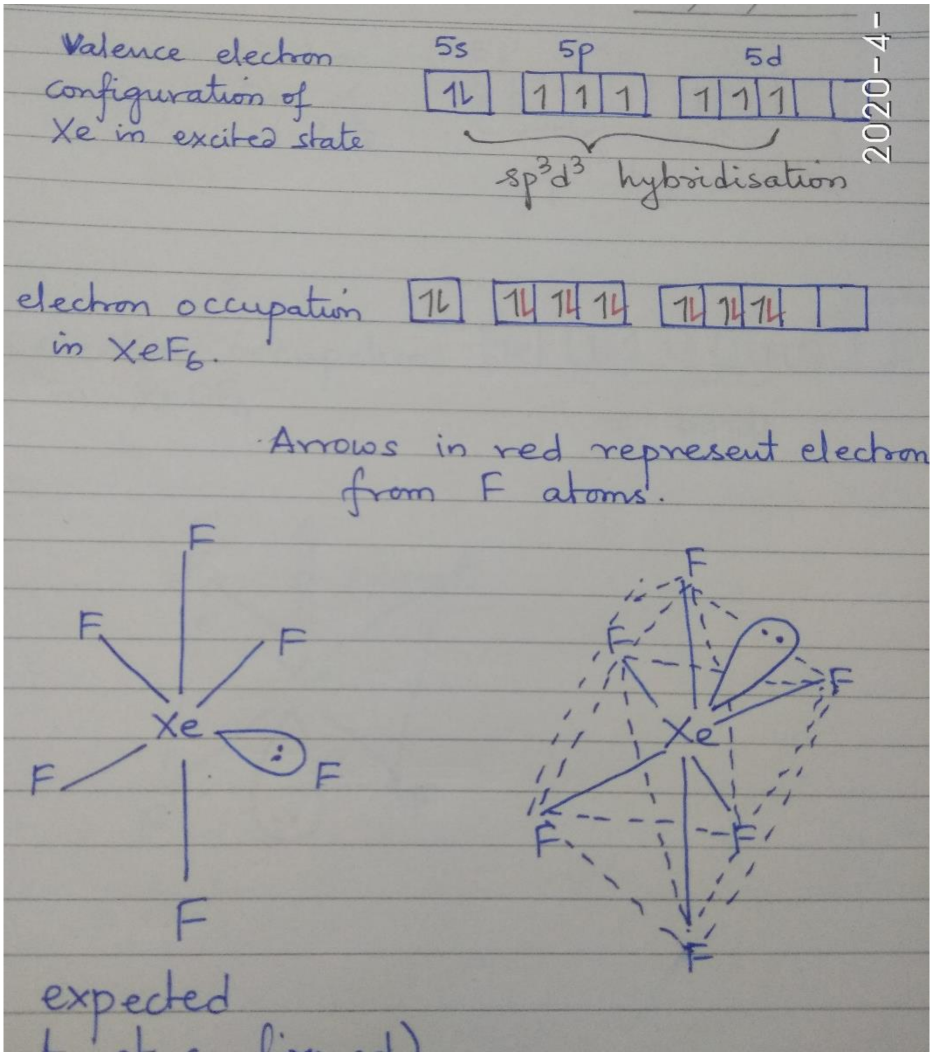
Hybridisation scheme for $XeOF_2$.

Xe(VI) compounds

(a) ***Xenon hexafluoride (XeF_6):*** Heating Xenon with excess fluorine (1:20 molar ratios) in a nickel vessel at 250-300 °C, under 50-60 atm. pressures, gives XeF_6.

$$Xe + 3F_2 \quad \rightarrow \quad XeF_6$$

In XeF_6, there are total 7 pairs of electrons {1/2(8+6)=7}, which should be accommodated around Xe in 7 orbitals. To do so, Xe undergoes, sp^3d^3 hybridisation to give 7 hybrid orbitals (one s +three p + three d) having 6 unpaired electrons and one lone pair. The six unpaired electrons form 6 sigma bonds with the unpaired electrons of the six F atoms. As the hybridisation is **sp^3d^3**, expected shape is pentagonal bipyramidal, with 6 fluorine atoms occupying 6 positions and the lone pair at one of the pentagonal position. But such a structure has not yet been confirmed. It has been suggested that the molecule has a ***distorted octahedral structure*** with 6 fluorine atoms at the vertices of the octahedron and the lone pair at the center of one of the triangular faces.



Hybridisation scheme and structure of XeF_6

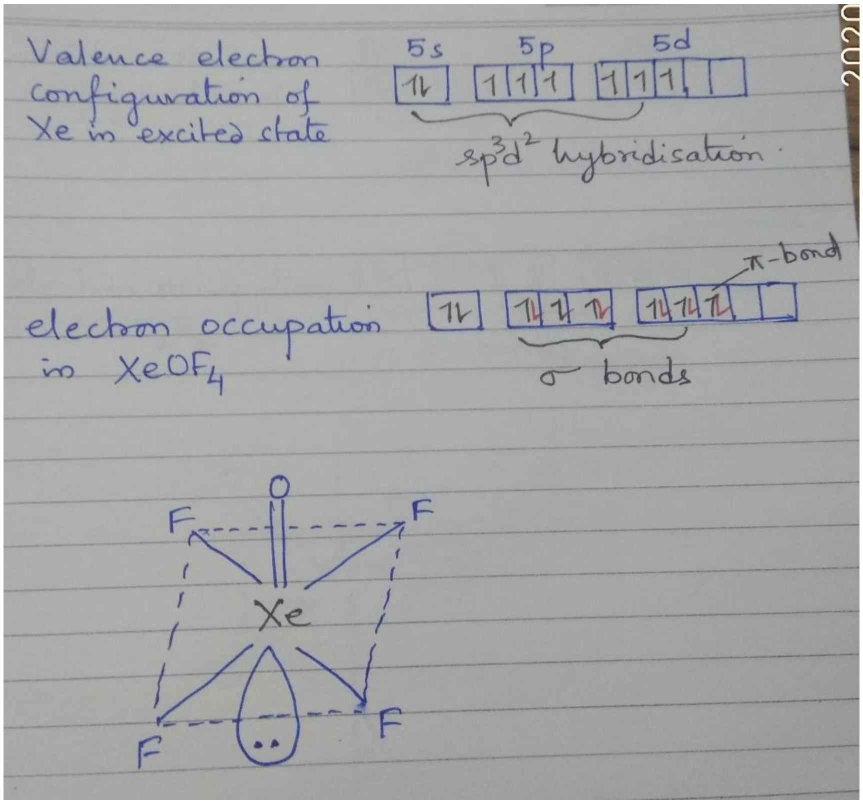
(b) ***Xenon Oxotetrafluoride ($XeOF_4$)***: Partial hydrolysis of XeF_6 gives $XeOF_4$ in small quantities.

$$XeF_6 + H_2O \quad \rightarrow \quad XeOF_4 + 2HF$$

Appreciable quantities of $XeOF_4$ is obtained by heating Xenon and Fluorine in 1:4 molar ratios in the presence of large excess of oxygen at ~230 ºC.

The molecule has a square pyramidal structure, which may be explained as follows.

Xe in its excited state transfers its three p- electrons into the three d- orbitals. The 5s orbital having lone pair electrons, three 5p orbitals having unpaired electrons and two 5d orbitals having unpaired electrons hybridise to give six **sp^3d^2** hybrid orbitals. Xe forms 4 sigma bonds with 4 fluorine atoms utilising four hybrid orbitals having unpaired electrons and one sigma bond with the O atom. The unhybridised d-orbital forms a π bond with another unpaired electron of the O atom. The 4 fluorine atoms occupy the corners of a square, while the O atom lies at one of the axial position of the octahedron and the lone pair, opposite to the O atom. If the lone pair position is ignored, the shape of the molecule is a ***square pyramid***.

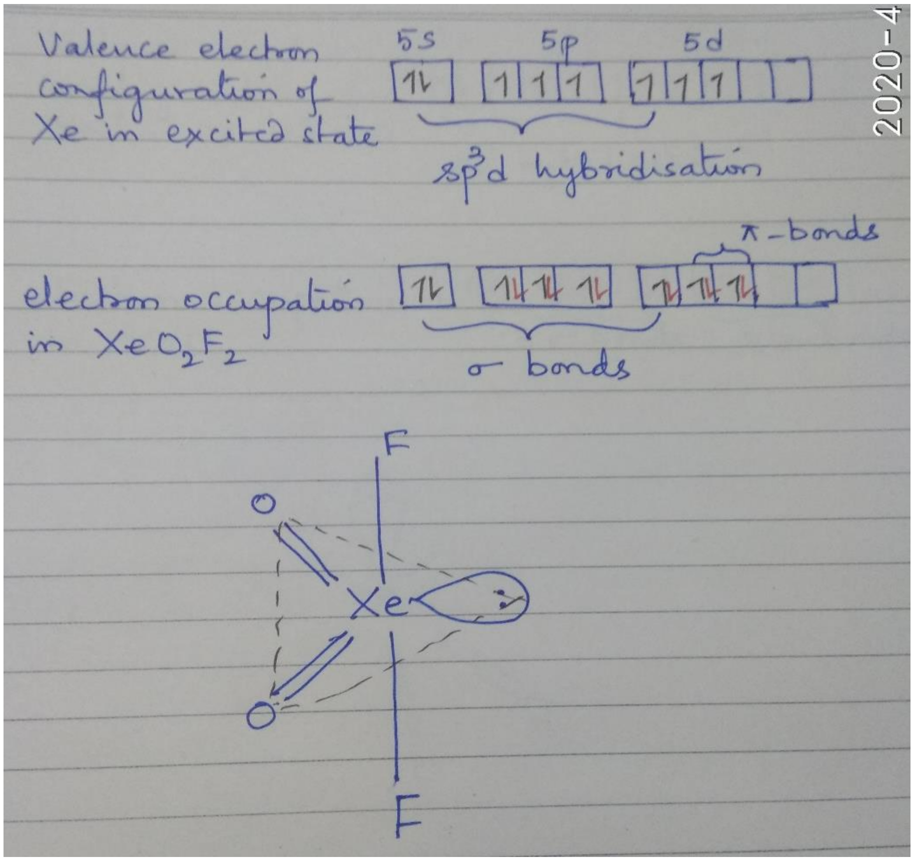


Hybridisation scheme and structure of $XeOF_4$

(c) ***Xenon dioxodifluoride (XeO_2F_2):*** Obtained when $XeOF_4$ reacts with silica.

$$2XeOF_4 + SiO_2 \longrightarrow XeO_2F_2 + SiF_4$$

The molecule has a trigonal bipyramidal structure with one lone pair at one of the equatorial position. The structure may be explained on the basis of **sp^3d** hybridisation of Xe valence orbitals. The three p-orbitals gets their electrons excited to the d- orbitals, which gives 7 orbitals (one s orbital with lone pair, 3 p- orbitals with unpaired electrons and 3 d-orbitals with unpaired electrons) in the excited state. Out of these 7 orbitals, one s, 3 p- and one d- orbital hybridise to give five sp^3d hybrid orbitals having a lone pair and 4 hybrid orbitals each with an unpaired electron. These 4 hybrid orbitals form four sigma bonds with two oxygen and two fluorine atoms. The unhybridised d- orbitals of Xe, overlap sideways with the other p- orbital of both the oxygen atoms and form two π bonds. Both the oxygen atoms and lone pair occupy the trigonal plane while the fluorine atoms occupy the pyramidal positions, giving a ***trigonal bipyramidal*** shape to the molecule.



Hybridisation scheme and structure of XeO_2F_2

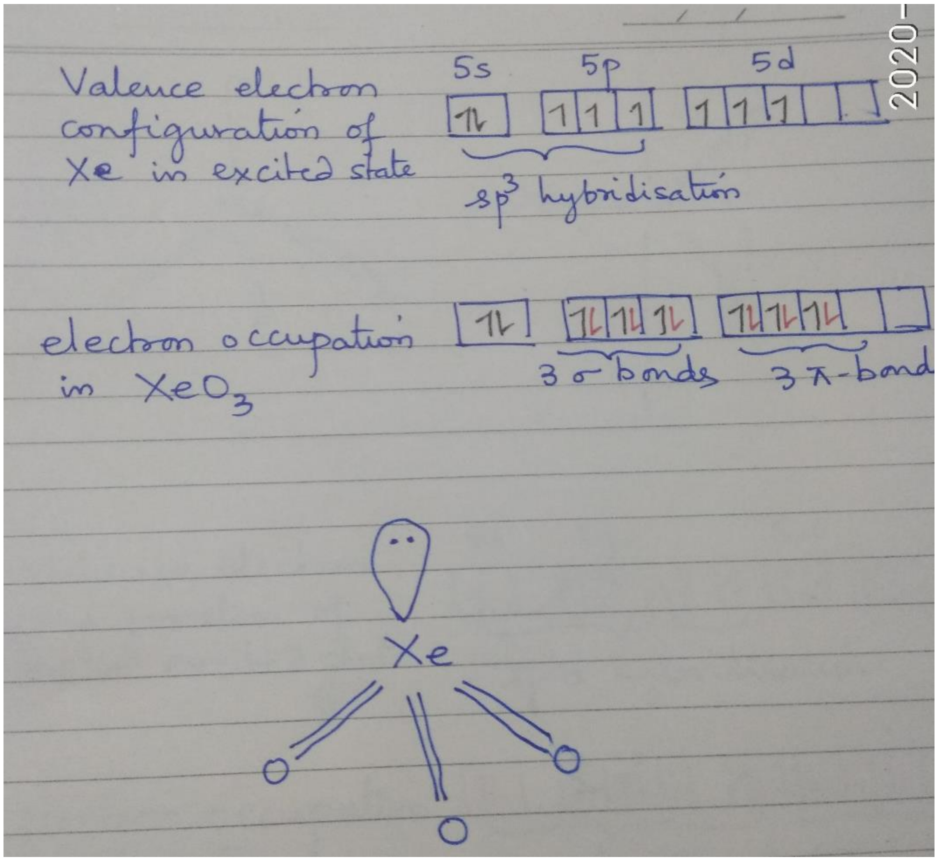
(d) ***Xenon trioxide (XeO_3):*** Xenon trioxide forms in small amounts when XeF_4 undergoes disproportionation on hybridisation with water.

$$2XeF_4 + 3H_2O \longrightarrow Xe + XeO_3 + 6HF + F_2$$

Also, when XeF_6 reacts slowly with atmospheric moisture, XeO_3 is obtained.

$$XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$$

XeO_3 has pyramidal structure, which may be explained based on the **sp^3** hybridisation of Xe valence orbitals. As before, the electrons in the p- orbitals get excited into the d- orbitals in the excited state. Xe then undergoes sp^3 hybridisation, which gives one orbital with lone pair and three orbitals having unpaired electrons each. Xe forms 3 sigma bonds with 3 oxygen atoms. The unhybridised d orbitals overlap sideways with the other p-orbital of the same oxygen atoms forming three π-bonds. The oxygen atoms occupy three of the tetrahedral corners around Xe, while the lone pair occupies the fourth corner, giving a ***pyramidal shape*** for the molecule.



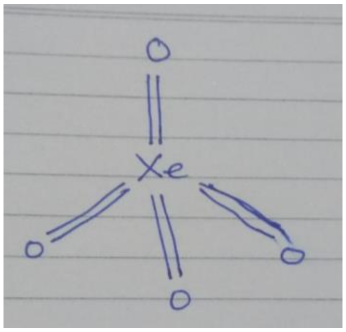
Hybridisation scheme and structure of XeO_3

Xenon(VIII) compounds

(a) Xenon tetraoxide (XeO_4): It is prepared from barium perxenate on treatment with anhydrous sulphuric acid. It is not very stableand decomposes to give xenon and oxygen.

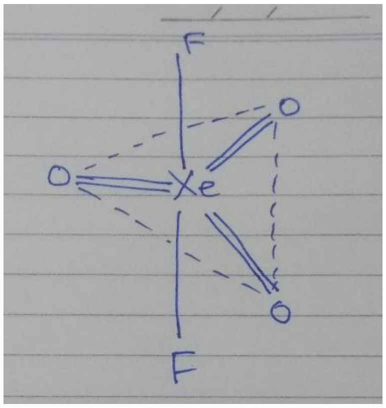
$$Ba_2XeO_6 + 2H_2SO_4 \longrightarrow XeO_4 + 2BaSO_4 + 2H_2O$$

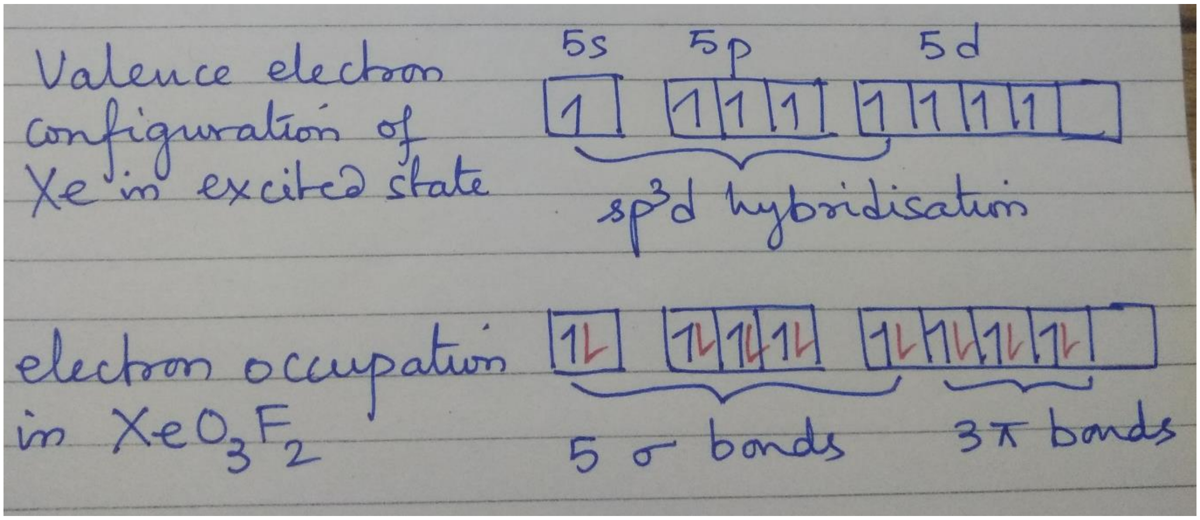
The structure of the molecule is ***tetrahedral***, which may be explained based on **sp^3** hybridisation of Xenon valence orbitals. (students may workout the hybridisation scheme).



Structure of XeO_4

(b) Xenon trioxodifluoride (XeO_3F_2): Though the compound is not well characterised, however, its structure is adequately confirmed. It has a ***trigonal bipyramidal*** geometry with three oxygen atoms (doubly bonded to central xenon) in the trigonal plane and two fluorine atoms (singly bonded to xenon) in the pyramidal positions. Such a structure may be explained on the basis of **sp^3d** hybridisation.

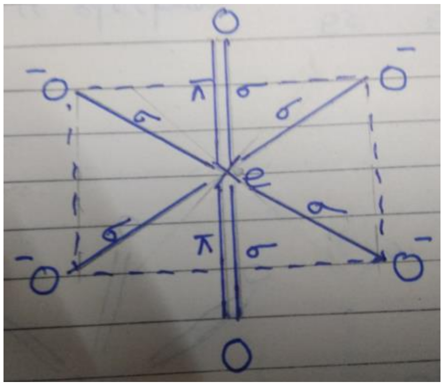




hybridisation scheme for XeO_3F_2

(c) ***Perxenate ion (XeO_6^{4-})***: When xenon trioxide is dissolved in aqueous sodium hydroxide, disproportionation takes place to give sodium perxenate ($Na_4XeO_6.8H_2O$). X-ray analysis reveals ***octahedral*** perxenate ion, with four oxygen atoms in the plane singly bonded to xenon, while the axial oxygens, are doubly bonded.

This structure may be explained based on the **sp^3d^2** hybridisation of Xe in the excited state. In the excited state, all the s- and p- electrons get excited to the d- level. This results in 8 unpaired electrons in the excited state of Xenon. Out of this, one s-, three p- and two d- orbitals hybridise to give six sp^3d^2 hybrid orbitals, which accept electrons from six oxygen atoms forming six sigma bonds. The unhybridised d- orbitals overlap sideways with the unpaired electrons of the axial oxygen atoms forming two π bonds.



hybridisation scheme in XeO_6^{4-}