B. Sc SEMESTER III
CHMMAJ201-4
Course Title : Inorganic Chemistry - I

Unit 3: Noble Gases

Introduction: The noble gases comprise of helium, neon, argon, krypton, xenon and radon. All these gases, except radon are present in the atmosphere. Radon results from the disintegration of radium and is radioactive itself.

These gases have highly stable $s^2 p^6$ electronic configurations in their outer (valency) shells and therefore, they have very little tendency to form chemical compounds with other elements.

The word "inert" for the noble gases is however inappropriate and now they are referred as "noble gases" where the word 'noble' signify that they enter into very few chemical reactions.

Occurence: The noble gases are rare gases and thus occur only as minor constituents in the atmosphere.

Gas	He	Ne	Ar	Kr	Xe
Percentage by Volume	5.24×10^{-4}	1.82×10^{-3}	9.34×10^{-1}	1.45×10^{-3}	8.70×10^{-6}

Electronic Configuration of Noble Gases: The atomic numbers of Group 18 elements are 2, 10, 18, 36, 54 and 86 respectively. Helium has the stable s^2 configuration. All of the other elements have highly stable $ns^2 p^6$ configuration in the outer (valency) shell.

Noble Gas	Atomic Number	Electronic Configuration	Configuration of outer shell
He	2	$1s^2$	$1s^2$
Ne	10	$1s^2 2s^2 p6$	$2s^2 2p6$
Ar	18	$1s^2 2s^2 2p^6 3s^2 3p6$	$3s^2 3p^6$
Kr	36	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p\ 6$	$4s^2 4p^6$
Xe	54	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6$	$5s^2 5p^6$
Rn	86	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10}$ $5s^2 5p^6 5d^{10} 4f^{14} 6s^2 6p^6$	$6s^2 6p6$

Uses of noble gases: 1) **Uses of Helium** : (i) Helium is used chiefly in filling lighter-than-air crafts such as air ships, weather balloons, etc. Although it is twice as heavy as hydrogen, its lifting power (which is determined by the difference between the density of air and the density of the balloon) is 92 percent of that of hydrogen. Helium is more safer than hydrogen because it is non-flammable.

(ii) Since He unlike N is not soluble in blood even under pressure a mixture of 80 percent He and 20 percent Oxygen is Used, instead of ordinary air, in modern diving apparatus. If air is Used as such in the diving apparatus, the N_2 dissolves in the blood of the diver due to high pressure when he is down in the deep sea. As soon as he comes to the surface, the pressure is released and the dissolved nitrogen escapes. This gives rise to coisson disease or the 'bends'. A similar helium-oxygen mixture is used to assist breathing in asthma and other respiratory diseases.

(iii) He, liquid helium (b.p 4.2K) is used as a cryogenic fluid to provide low temperatures for studying a number of phenomena which occur near absolute zero.

Uses of neon : (i) Neon has a characteristic property of giving an orange-red glow in a discharge tube at low pressure (2mm) at 1000 volts. It is therefore, intensively used in neon glow lamps (commonly known as neon tubes) for advertising purposes.

If mercury vapours are mixed with neon, a glow of blue or green colour is obtained.

Uses of argon: (i) Argon is used for filling incandescent metal filament electric bulbs. Its action there is to prevent the volatisation of the tungsten filament at the high temperature of the lamp.

(ii) It is chiefly employed in welding and other operations which require absence of nitrogen as well as a non-oxidising atmosphere.

Uses of Krypton and Xenon : Krypton and Xenon are also used in filling incandescent metal filament electric bulbs.

Radon : It has not found any important industrial application so far. However, it has been used in the treatment of cancer.

Physical Properties of noble gases

(i) Melting points and boiling points : It is seen that boiling as well as melting points of noble gases are very low. This is due to very weak intermolecular (vander Waals) forces of attraction in these gases. The melting and boiling points of helium are the lowest of any known element. Melting points and boiling points increase regularly when we move down the group.

(ii) Liquefaction : The noble gases are liquefied with great difficulty. This is indicated by their very low critical temperatures. This is again because of weak ~~va~~ vander Waals or intermolecular forces existing in these gases. Heat of vaporisation is also low.

ii) Solubility in water : These gases are only slightly soluble in water (8 to 40 ml per litre at 25°C). The solubility, in general, increases with increasing molar mass.

(iv) Ionisation energies and electron affinities : The ionisation energies of these elements are quite high. The values however, decrease with increasing molar mass. The electron affinities are close to zero.

(V) Mono-atomicity : The gases exist as monoatomic molecules since their atoms are not capable of combining even amongst themselves.

Compounds of Noble gases

1) Hydrates : (i) Hydrates of noble gases are formed by compressing the gases in water.

(ii) Deuterates are also formed by compressing the gases in heavy water.

(iii) The hydrates and deuterates of the heavier noble gases are known to be more stable. Thus, $Xe \cdot 6H_2O$ is the most stable hydrate of a noble gas.

2) Clathrates of Noble Gases : Noble gases form a number of compounds in which the gases are trapped within cavities of crystal lattices of certain organic and inorganic substances. Such compounds are known as clathrates. These are also referred to as cage compounds.

Example : When β- quinol (o-dihydroxy benzene) is allowed to crystallise from its solution in water in the presence of a heavier noble gas get trapped within the lattice of quinol crystals. In other words, the crystals obtained are not of quinol but of a clathrate compound of the noble gas with quinol. The crystals are quite stable and can persist for several years.

However, when heated or dissolved in water, the gas escapes and quinol remains behind as such.

Properties: (i) X-ray examination shows that a crystal of β-quinol is a three-dimensional network containing several cavities of 4Å diameter, the quinol molecules being bound together with hydrogen bonds.

β-quinol is allowed to crystallise from its solution in the presence of any foreign atom or molecule of suitable size which can fit in the cavities tightly, a clathrate compound results.

(ii) The trapped atoms or molecules are unable to escape. If the molecules are too small, as those of helium and neon, they are able to escape easily from the cavities. Thus, He and Ne do not form clathrate compounds with quinol. Argon, krypton and Xenon molecules on the other hand, are of suitable sizes and form these compounds.

Uses of clathrates: a) Clathrates of argon, krypton and Xenon provide convenient means of handling and transporting isotopes of these gases.

b) Krypton ^{85} clathrate provides a safe source for β-radiations while Xenon $^{\#133}$ clathrate provides a useful source for γ radiations.

Preparation and Properties of XeF_2, XeF_4 and XeF_6

Some stable Compounds of Xenon with Fluorine and Oxygen in Different Oxidation States of Xenon

Oxidation State of Xenon	Compounds of Xenon
2	XeF_2
4	XeF_4, $XeOF_2$
6	XeF_6, $XeOF_4$, XeO_2F_2, XeO_3
8	XeF_8, XeO_4, XeO_3F_2, XeO_2F_4

Xenon (II) Compounds

1) Xenon Difluoride, XeF_2, Preparation:

Xenon difluoride is best prepared by heating a mixture of xenon and fluorine in molecular ratio of 2:1 at 400°C in a sealed nickel tube. On cooling quickly, a colourless solid XeF_2 results.

$$Xe + F_2 \xrightarrow[400^\circ C]{Ni} XeF_2$$

Alternatively, the 1:1 mixture of xenon and fluorine may be subjected to electric discharge to get xenon difluoride.

2) It is also formed by photochemical combination of xenon and fluorine under the influence of mercury vapour

$$Xe + F_2 \xrightarrow{Hg\ vapour} XeF_2$$

3) ~~X~~ It can also be prepared by fluorination of xenon by oxygen monofluoride (O_2F_2) at -178°C.

$$Xe + O_2F_2 \xrightarrow{-178^\circ C} XeF_2 + O_2$$

Properties: 1) Xenon difluoride is a colourless, crystalline Solid which melts at 140°c

2) It dissolves in hydrogen fluoride without reacting with it

3) It reacts with hydrogen to give xenon and hydrogen fluoride

$$XeF_2 + H_2 \rightarrow Xe + 2HF$$

4) It reacts with water evolving oxygen

$$2XeF_2 + 2H_2O \rightarrow 2Xe + 4HF + O_2$$

5) It oxidises iodine in the presence of BF_3 to give IF

$$XeF_2 + I_2 \xrightarrow{BF_3} 2IF + Xe$$

6) It reacts with sulphur trioxide to give xenon

$$XeF_2 + 2SO_3 \rightarrow Xe + S_2O_6F_2$$

7) It is a mild fluorinating agent. Thus, it reacts with benzene to give fluorobenzene, C_6H_5F

8) It is also a strong oxidizing agent. It oxidises HCl to Cl_2 and Ce(III) to Ce(IV)

9) In BrF_3 solution, xenon difluoride donates F^- to MF_5 (where M = P, As, Sb, etc)

$$XeF_2 + SbF_5 \rightarrow [XeF]^+[SbF_6]^-$$

$$2XeF_2 + AsF_5 \rightarrow [Xe_2F_3]^+[AsF_6]^-$$

10) It reacts with anhydrous HSO_3F, $HClO_4$, CF_3COOH to give mixed fluoro-oxy compounds $FXeOSO_2F$, $FXeOClO_3$, $FXeOOCCF_3$, respectively.

11) It reacts with $\cdot CF_3$ in vapour phase to give $Xe(CF_3)_2$ which contains Xe–C bond.

$$C_2F_6 \xrightarrow{plasma} 2\cdot CF_3$$

$$2\cdot CF_3 + XeF_2 \rightarrow Xe(CF_3)_2 + F_2$$

12) It reacts with $HN(SO_2F)_2$ in CF_2Cl_2 to give $F-Xe-N(SO_2F)_2$

$$XeF_2 + HN(SO_2F)_2 \rightarrow F-Xe-N(SO_2F)_2 + HF$$

Structure of XeF_2 molecule: Spectroscopic analysis has shown that XeF_2 molecule has linear geometry. This is explained on the basis of VSEPR theory as follows:

In the formation of XeF_2 molecule, one of the 5p electrons in Xenon is assumed to shift to the 5d orbital so that there are two unpaired electrons. (one in 5p and one in 5d orbital) in the excited state of Xenon. One 5s, three 5p and one 5d orbitals hybridise to give sp^3d hybrid orbitals. The two sp^3d hybrid orbitals of Xenon containing single electrons overlap with the half-filled p orbitals of the two fluorine atoms forming two Xe-F sigma bonds. The Xenon and the two fluorine atoms lie in a straight line (i.e are linear) while the three equatorial positions are occupied by the three lone pairs of electrons to minimise electron pair repulsions (VSEPR) theory.

The molecule thus has linear geometry as shown in figure below.

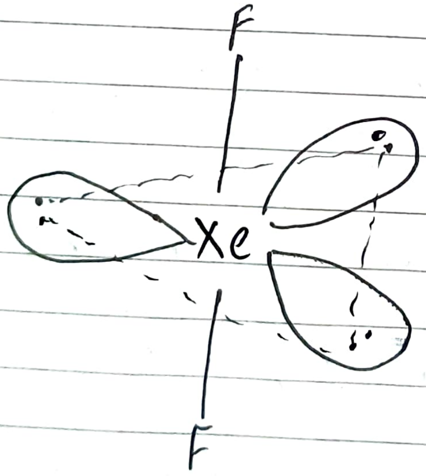


Fig: The structure of XeF_2 molecule.

2) Xenon (IV) compounds:

1. Xenon Tetrafluoride, XeF_4:

Preparation: 1) It is prepared by passing a mixture of xenon and fluorine, in the molecular ratio of 1:5, through a nickel tube, at 400°C under a pressure of 5-6 atm

$$Xe + 2F_2 \xrightarrow[5-6 atm]{400^\circ C} XeF_4$$

~~2) It is also sy-~~

2) It is also synthesised by passing an electric discharge through a mixture of xenon and fluorine in the molecular ratio of 1:2 at −80°C.

Properties: 1) It is a colourless, crystalline solid which melts at 117.1°C. It sublimes readily.

2) It dissolves in hydrogen fluoride without reacting.

3) It is reduced by hydrogen at 117°C to give xenon.

$$XeF_4 + 2H_2 \longrightarrow Xe + 4HF$$

4) It reacts with boron trichloride to form boron trifluoride

$$3XeF_4 + 4BCl_3 \longrightarrow 4BF_3 + 3Xe + 6Cl_2$$

5) It undergoes disproportionation in water giving a highly explosive solid compound, XeO_3.

$$2XeF_4 + 3H_2O \longrightarrow Xe(g) + XeO_3(s) + 6HF(aq) + F_2(g)$$

But, if the reaction is carried out at −80°C, it forms xenon oxofluoride.

$$XeF_4 + H_2O \xrightarrow{-80^\circ C} XeOF_2 + 2HF$$

6) It combines with molten TaF_5 to form a straw-coloured compound, $Xe(TaF_6)_2$.

$$XeF_4 + 2TaF_5 \longrightarrow Xe(TaF_6)_2 + F_2$$

7) It is a stronger fluorinating agent than XeF_2. It converts Hg to Hg_2F_2, Pt to PtF_4, NO and NO_2 to NOF and NO_2F, SF_4 to SF_6 etc. Thus,

$2Hg + XeF_4 \longrightarrow Xe + 2HgF_2$
$Pt + XeF_4 \longrightarrow Xe + PtF_4$
$2SF_4 + XeF_4 \longrightarrow Xe + 2SF_6$

8) It forms an addition compound with antimony pentafluoride.

$XeF_4 + SbF_5 \longrightarrow XeF_4 \cdot SbF_5 \longrightarrow [XeF_3]^+[SbF_6]^-$

Structure of XeF_4 molecule: The structure of XeF_4 molecule can be explained as follows:

Since no double bonds are formed in the structure of XeF_4, the number of valence electron pairs around Xe atom would be $\frac{1}{2}(8+4) = 6$ (four electrons come from the four covalently bonded fluorine atoms).

In the formation of xenon tetrafluoride, two of the 5p electrons go to the 5d orbitals so that there are now four unpaired electrons (two in 5p and two in 5d orbitals). The six orbitals (one 5s, three 5p and two 5d) of Xe hybridise to form six sp^3d^2 hybrid orbitals. The covalent bonds are formed by overlapping of four of these hybrid orbitals (each containing a single electron) of Xenon with half-filled p orbitals of fluorine atoms. The molecule has a square planar structure as shown in Fig 5. The two lone pairs occupy axial positions ~~so~~ so as to minimise electron pair repulsion (VSEPR theory). The xenon and the four fluorine atoms are coplanar.

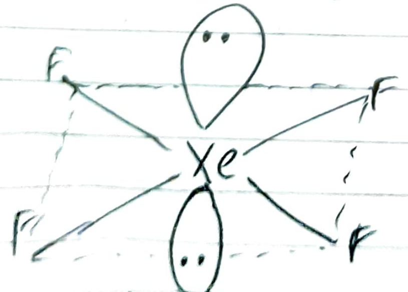


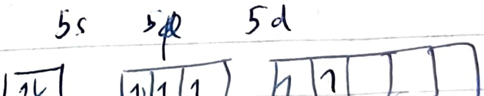
Fig 5: The structure of XeF_4 molecule.

2. Xenon ~~Oxof~~ Oxodifluoride, $XeOF_2$: It is prepared by slow and partial hydrolysis of XeF_4 at a low temperature (−80°c)

$$XeF_4 + H_2O \xrightarrow{80^\circ c} XeOF_2 + 2HF$$

It is not a very stable compound.

Structure of $XeOF_2$ molecule: Two 5p electrons of Xe are assumed to go to the 5d orbitals when Xe atom is in excited state. The five orbitals (one s, three p and one d) of Xe atom hybridise to form five sp^3d hybrid orbitals. Three of the five hybrid orbitals which are singly filled are used in forming sigma bonds with two fluorine atoms and one oxygen atom. One 5d orbital which is not involved in hybridisation and is singly filled is used in forming an additional bond, which is a pi bond, with the oxygen atom. There is thus a double bond (one sigma bond and one pi bond) between xenon and oxygen atoms. The two lone pairs of electrons occupy two equatorial positions to minimise electron pair repulsions. The compound therefore, has a T-shaped structure.



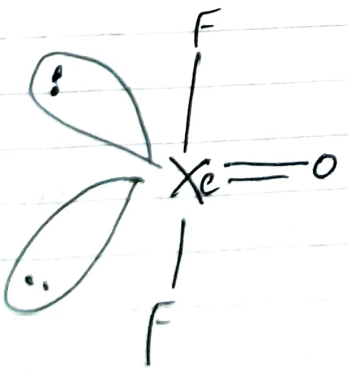


Fig: The T-shaped structure of $XeOF_2$ molecule.

In the case of $XeOF_2$ molecule, the number of Xe orbitals involved in hybridisation is calculated by ignoring the contribution of doubly bonded oxygen and taking into consideration the contribution of only the fluorine atoms bonded to the central atom by sigma bonds. Accordingly, the number of orbitals involved in hybridisation $= \frac{1}{2}(8+2) = 5$. Thus, the molecule involves sp^3d hybridisation of Xe orbitals.

Xenon (VI) compounds.

1. Xenon Hexafluoride, XeF_6

Preparation : a) It is prepared by heating Xenon with excess of fluorine (in the ratio of 1:20) in a nickel vessel at 250 – 300°C under a pressure of 50 – 60 atm.

$$Xe + 3F_2 \rightarrow XeF_6$$

b). It can be obtained by interaction of XeF_4 and F_2 under pressure.

$$XeF_4 + F_2 \rightarrow XeF_6$$

c) It is also prepared by passing electric discharge throu a mixture of Xenon and fluorine in the ratio of 1:3 at a low temperature.

Properties : 1. It is a crystalline solid which melts at 49.5

2. It is most volatile of all the fluorides of Xenon. Its vapours have a greenish yellow colour.

3. It dissolves in hydrogen fluoride giving a solution which is a good conductor of electricity. This is attributed to the formation of ions, as shown below.

$$HF + XeF_6 \rightarrow XeF_5^+ + HF_2^-$$

4. It is extremely reactive. It cannot be stored in glass or quartz vessels due to the following reactions

which finally give the dangerously explosive xenon trioxide.

$2XeF_6 + SiO_2 \rightarrow 2XeOF_4 + SiF_4$
$2XeOF_4 + SiO_2 \rightarrow 2XeO_2F_2 + SiF_4$
$2XeO_2F_2 + SiO_2 \rightarrow 2XeO_3 + SiF_4$
(explosive)

5. It is reduced to xenon by the action of H_2, NH_3 or HCl.

$XeF_6 + 3H_2 \rightarrow Xe + 6HF$
$XeF_6 + 8NH_3 \rightarrow Xe + 6NH_4F + N_2$
$XeF_6 + 6HCl \rightarrow Xe + 3Cl_2 + 6HF$

6. It undergoes slow hydrolysis with atmospheric moisture producing highly explosive XeO_3.

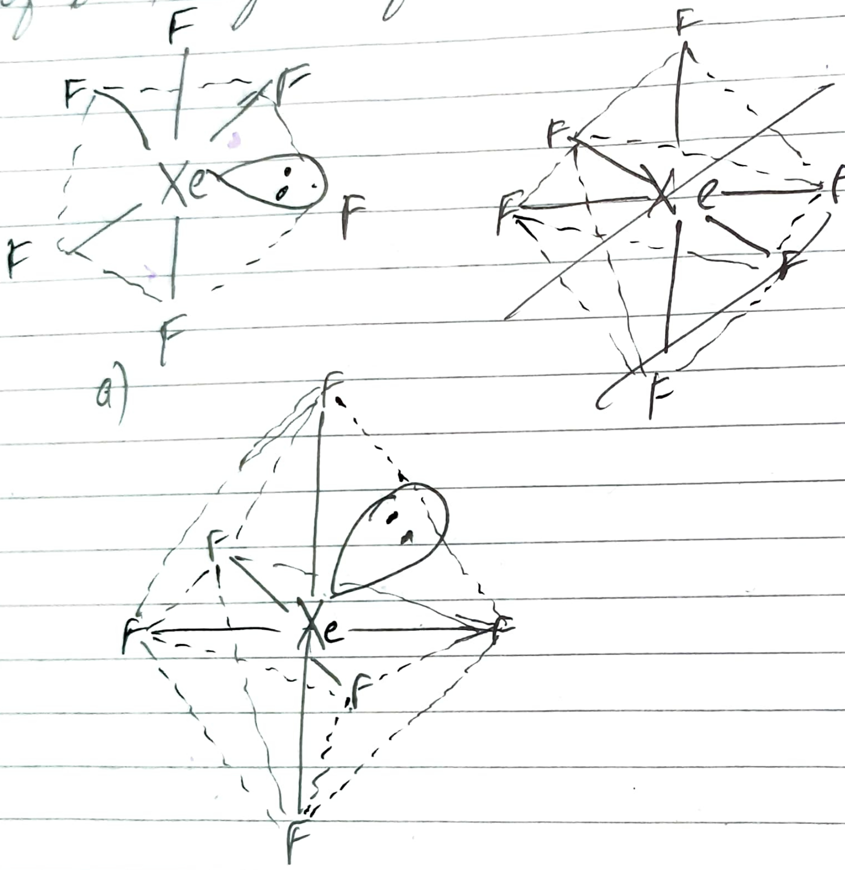
$XeF_6 + 3H_2O \rightarrow XeO_3 + 6HF$

7. It reacts with fluoride ion acceptors to form adducts.

$XeF_6 + SbF_5 \rightarrow [XeF_5]^+ [SbF_6]^-$
$XeF_6 + AsF_5 \rightarrow [XeF_5]^+ [AsF_6]^-$

Structure: In this case, the number of orbitals around the Xe atom would be $\frac{1}{2}(8+6) = 7$. ~~In the formation of XeF_6 molecule~~. In the formation of XeF_6 molecule, three of the 5p electrons of Xe move into the 5d orbitals so that 6 unpaired electrons (three in 5p orbitals and three in 5d orbitals) become available for chemical bonding. Thus, seven orbitals (one s, three p and three d) hybridise to give seven sp^3d^3 hybrid orbitals. Six of these orbitals containing a single electron each are used in bonding with six atoms of fluorine. The seventh hybrid orbitals accomodates a lone pair of electrons.

Due to sp^3d^3 hybridisation, the molecule should have pentagonal bipyramidal structure, with a lone pair of electrons at one position, as shown in fig below. However, this structure has not yet been confirmed. There has been controversy regarding its structure since its discovery. It has been suggested that the molecule has a distorted octahedral structure in which all the six positions are occupied by fluorine atoms and the lone pair is present at the centre of one of the triangular faces.



a)

b)

Fig: a) and b): The two possible structures

2. Xenon Oxotetrafluoride, $XeOF_4$.

Preparation : Xenon oxotetrafluoride is formed to a small extent by partial hydrolysis of Xenon hexafluoride.

$$XeF_6 + H_2O \longrightarrow XeOF_4 + 2HF$$

Properties : 1. It is a colourless compound melting at -46°C

2. On treatment with hydrogen it is reduced to xenon.

$$XeOF_4 + 3H_2 \longrightarrow Xe + H_2O + 4HF$$

3. It reacts with water to form oxofluoride, XeO_2F_2, in which xenon remains in the same oxidation state. This compound is named xenon dioxodifluoride

$$XeOF_4 + H_2O \longrightarrow XeO_2F_2 + 2HF$$

4. It also reacts with silica to yield xenon dioxodifluoride

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

Structure : Here, three of the 5p electrons are supposed to move to 5d orbitals when excited. The formation of the compound involves hybridisation of six Xe orbitals. These are 5s, all the three 5p and two of the 5d orbitals. This is thus a case of sp^3d^2 hybridisation of Xe orbitals.

Five of the singly occupied hybrid orbitals are involved in sigma bond formation with four fluorine atoms and one oxygen atom. The 5d orbitals which does not take part in hybridisation, forms a pi bond with the oxygen atom. Thus oxygen is combined to Xenon by a double bond, one of which is a sigma bond and the other is a pi bond. It may be noted that one of ~~which is a sigma bond and the~~

the hybridised orbital contains a lone pair of electrons. The molecule has a square pyramidal structure. The fluorine atoms are coplanar, i.e, lie in the same plane. The lone pair of electrons lies opposite to the oxygen atom which is bonded to Xenon atom by a double bond. This is to minimise electron pair repulsion.

The number of orbitals involved in hybridisation in this case would be $\frac{1}{2}(8+4) = 6$.

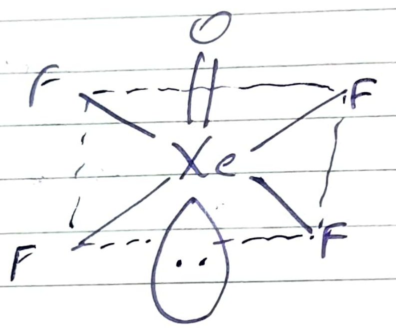


Fig: The structure pyramidal structure of $XeOF_4$ molecule.

3. Xenon dioxofluoride, XeO_2F_2 ;

Structure : In this compound, three of the 5p electrons of Xe are supposed to move into 5d orbitals when excited. There are 5s, all of the three 5p orbitals and one of the 5d orbitals resulting into sp^3d hybridisation.

The four hybrid orbitals are involved in sigma bond formation with two fluorine atoms and two oxygen atoms. The remaining two singly filled orbitals which do not take part in hybridisation, form pi bonds with the same two oxygen atoms. The remaining hybrid orbital contains a lone pair of electron.

According to the empirical rule also, the number of electrons around Xe atom to be accomodated in hybrid orbitals is $\frac{1}{2}(8+2)=5$ (contribution due to doubly bonded O atoms is to be ignored as per rule).

Therefore, the hybridisation of Xe orbitals is sp^3d.

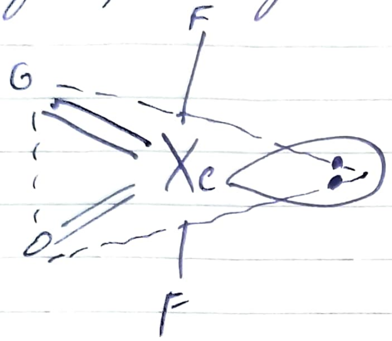


Fig: The distorted trigonal bipyramidal structure of XeO_2F_2 molecule.

4. Xenon Trioxide, XeO_3

In the formation of XeO_3, three of the 5p electrons of Xe are supposed to move to 5d orbitals when excited. The formation of XeO_3 molecule thus involves sp^3 hybridisation of the orbitals of Xe.

Three of the four hybrid orbitals which are singly filled, form three sigma bonds with three oxygen atoms. The three 5d orbitals which are excluded from hybridisation, form three pi bonds with the same three oxygen atoms. Thus, each atom of oxygen is bonded to Xenon by a double bond. One of the hybrid orbitals of Xe contains a lone pair of electrons. The molecule has a pyramidal structure.

The empirical rule also suggests sp^3 hybridisation since the number of orbitals involved in hybridisation would be $\frac{1}{2}(8+0)=4$

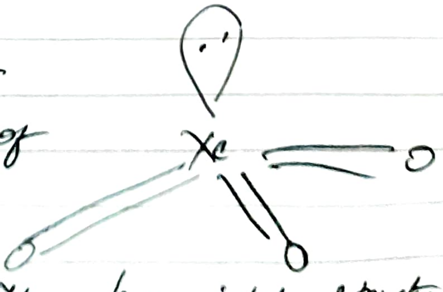


Fig: The pyramidal structure of XeO_3 molecule.