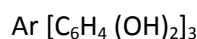


NOBLE GAS CHEMISTRY (Group-18)

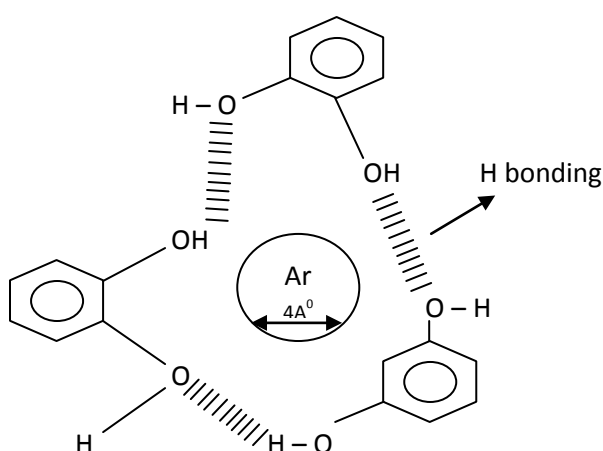
Q. What are Clathrates or cage compounds or host-guest compounds? Give one example.

Ans: $C_6H_4(OH)_2 + Ar$ (18 – 42 atm pressure)

↓ **Crystallisation**



(Clathrates compound)



Clathrates compounds are the compounds in which some atoms or molecules (e.g. inert gas) which are capable of independent existence are trapped in the cavities of the crystal structure of some organic or inorganic compounds. The atom or molecules **are purely physically trapped** and no chemical bonding or interaction except weak the vander Waal's force is present in the crystal structure. The atoms or molecules which are trapped are called guest moieties and the compound whose crystal structure provides the accommodation of guest moieties are called host moieties.

ESSENTIAL CONDITION FOR FORMATION:

1. Presence of cavities of appropriate size in the crystal lattice of the host.
2. Size of the guest particle should be such as to fit in the cavities of the host.

Stability:

Clathrate compounds once formed are quite stable due to the following reasons:

- (a) The guest molecules tightly fit in the cavities of the host molecules.



(b) The guest molecules within the cages are at a minimum potential energy.

The guest can escape from the host only when the forces holding the molecular cages together are overcome. This can be achieved by the following two methods:

(i) By heating the crystals.

(ii) By dissolving them in a suitable solvent such as alcohol.

Uses:

1. In the separation of noble gases, for example, neon can be separated from Ar, Kr and Xe because neon is the only gas which does not form clathrates with quinol.
2. Krypton – 85 clathrate provides a safe and useful source of β radiations which are useful for measuring thickness of gauges.
3. Xe – 133 clathrates provides a compact source of γ radiations.

Q. Which is the most abundant noble gas in the universe? Write its uses.

Ans: Helium (He) is the most abundant noble gas in the universe.

Uses:

1. Helium being lighter and inflammable it is used for filling air ships and weather balloons.
2. A mixture of He and O_2 is used by deep sea divers for respiration.

Q. Which is the most abundant noble gas in air? Write its use.

Ans: Argon is the most abundant noble gas in air.

Uses:

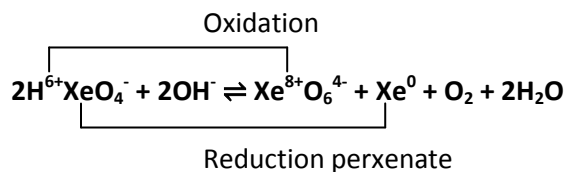
1. It is used for filling incandescent metal filament in electrical bulbs. Its action is to prevent the volatilisation of tungsten filament at high temperature.
2. It is used for welding and other operations which require absence of nitrogen as well as a non-oxidising atmosphere.

Q. The xenate ion disproportionates in basic solution to yield xenon and perxenate ion. Give the balanced equation.

Ans:
$$XeO_3 + OH^- \rightleftharpoons HXeO_4^- \text{ (xenate ion)}$$



The xenate ion slowly disproportionate to generate perxenate ion, xenon and oxygen gas

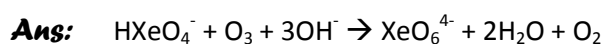


Q. What was the chemistry behind the synthesis of the first noble gas compound XePtF₆?

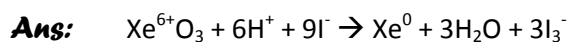
Ans: N. Bartlett observed that PtF₆ changes its colour on exposure to air. It was subsequently observed that, PtF₆ is a very strong oxidising agent and is capable to oxidise O₂ to produce O₂⁺. Since ionisation energy of Xe is also comparable to that of O₂ so it is natural to expect that PtF₆ may oxidise Xe too. In fact Bartlett reported an orange solid on reacting Xe with PtF₆ and it is formulated as XePtF₆. This was beginning of noble gas chemistry.

Q. Write the balanced equation for the following:

(a) Oxidation of HXeO₄⁻ by ozone.



(b) Reduction of XeO₃ by iodide in acid medium to xenon.



Q. Suggest the most suitable noble gas for each of the following uses.

Ans: (i) Providing the least expensive inert atmosphere: **Argon**

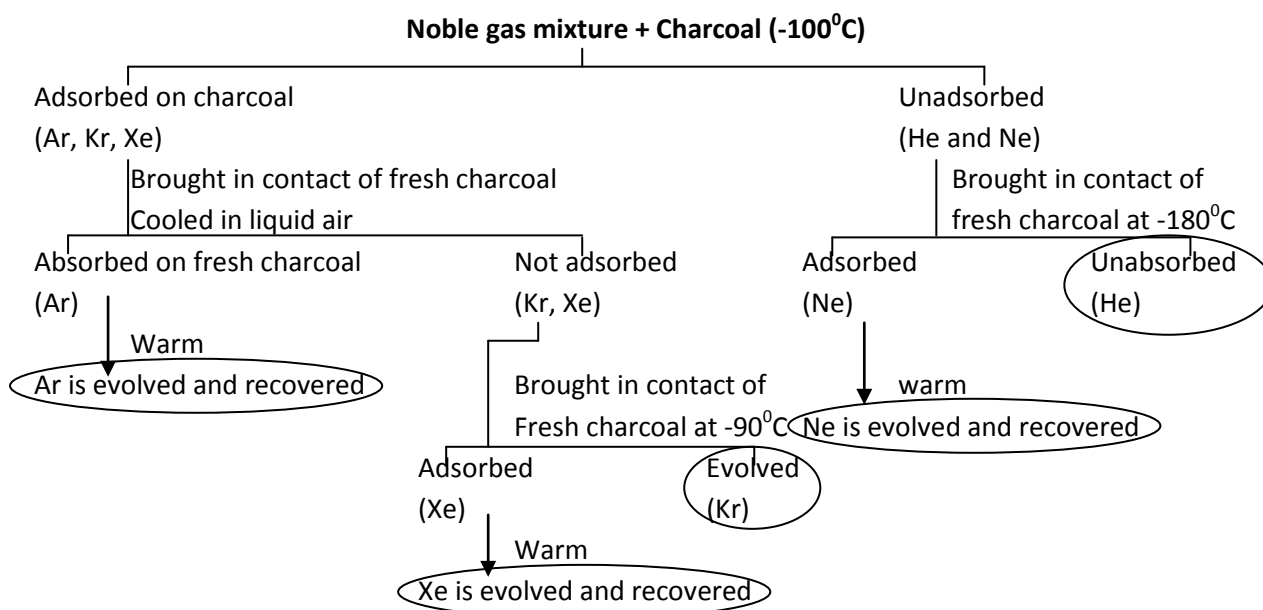
(ii) A very low temperature liquid refrigerant: **Helium**

(iii) An electric discharge light source using a safe gas with low IE: **Xenon**.

Q. Write notes on isolation of noble gas.

Ans: The first step involves the removal of nitrogen and oxygen of the atmosphere as NO₂. Then the noble gases are separated by using Dewar's method, which is based on differential adsorption of these noble gases by charcoal. In this method, the mixture is kept into a bulb containing coconut charcoal and placed in a cold bath (-100°C) in a Dewar flask. It is allowed to remain there for about an hour. Different gases are separated at different temperatures.





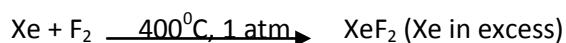
Q. Why most of those compounds involve only fluorine and oxygen?

- *Ans my class Lecture....SRC*

CHEMISTRY OF XENON DIFLUORIDE (XeF₂)

Preparation:

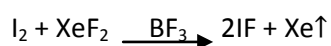
It is best prepared in the laboratory in high yields and purity by heating xenon and fluorine in the molar ratio of 2:1 (excess of xenon is taken to avoid the formation of xenon tetrafluoride). The reaction is carried out in a nickel vessel at 400°C. The reaction products are brought to room temperature and XeF₂ is isolated by vacuum sublimation.

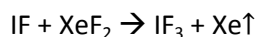


Properties:

XeF₂ has strong oxidising and fluorinating power. In all fluorinating reaction and oxidation reaction the first step involves the ionisation of XeF₂ to XeF⁺ followed by electron transfer to give XeF. The XeF species is very weakly bound and is potential source of fluorine atoms.

1. XeF₂ oxidises iodine in the presence of fluoride ion acceptor to give IF.





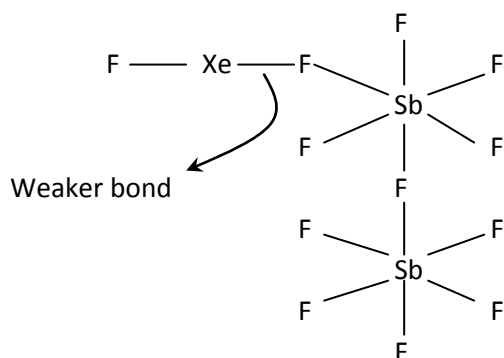
2. It reacts with NO to give nitrosyl fluoride



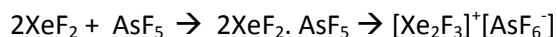
3. $\text{XeF}_2 + \text{SbF}_5 \rightarrow \text{XeF}_2 \cdot \text{SbF}_5 \rightarrow \text{XeF}^+ \text{SbF}_6^-$ (solid)

4. $\text{XeF}_2 + 2\text{SbF}_5 \rightarrow \text{XeF}_2 \cdot 2\text{SbF}_5 \rightarrow [\text{XeF}^+] [\text{Sb}_2\text{F}_{11}^-]$

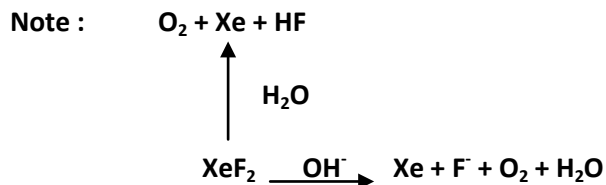
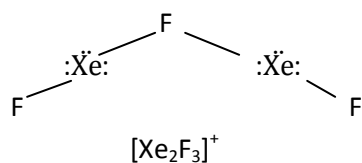
XeF^+ is strongly bonded to $\text{Sb}_2\text{F}_{11}^-$ by a fluorine bridge.



5. XeF_2 also reacts with AsF_5 in a different stoichiometry.



The ion Xe_2F_3^+ has the expected linear geometry around xenon and an angular geometry at the central fluorine.



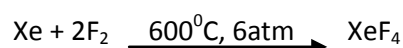
STRUCTURE AND BONDING :

Please see the last few pages

CHEMISTRY OF XENON TETRAFLUORIDE (XeF₄)

Preparation:

It is prepared in high yield by heating a mixture of xenon and fluorine in a molar ratio 1:5 at 400°C and 5-6 atm in an enclosed nickel vessel. The sample is purified by fractionation.

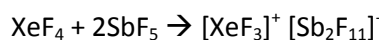
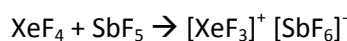


Reactions:

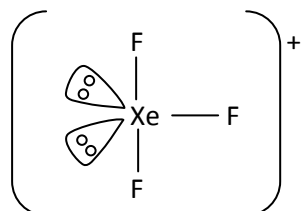
1. XeF₄ reacts with boron trichloride to give boron trifluoride.



2. XeF₄ forms an addition compound with antimony pentafluoride

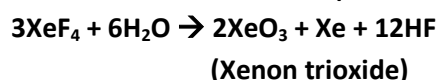
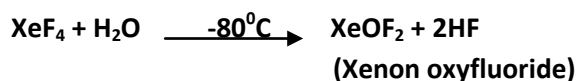


The XeF₃⁺ ions have the expected T shaped structure.



3. Hydrolysis:

It is readily hydrolysed by water. The reaction can be controlled to yield different products.

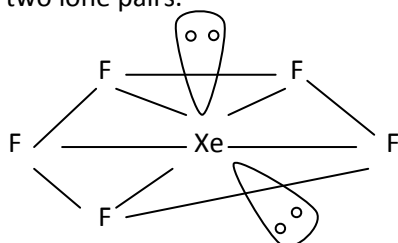


4. It forms stable 1:1 adduct with Lewis bases; such as Me₄N⁺F⁻ (tetra methyl ammonium fluoride) and alkali metal fluorides.



- (i) $\text{Me}_4\text{N}^+\text{F}^- + \text{XeF}_4 \rightarrow [\text{Me}_4\text{N}^+] [\text{XeF}_5^-]$
- (ii) $\text{MF} + \text{XeF}_4 \rightarrow \text{M}^+ [\text{XeF}_5^-]$ $[\text{M} = \text{Na}^+, \text{K}^+, \text{Rb}^+, \text{Cs}^+]$

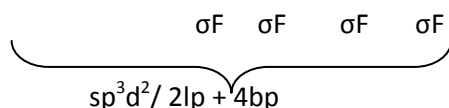
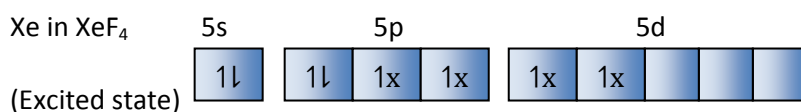
The XeF_5^- anion shows the most unusual **pentagonal planar** structure in which two axial positions are occupied by two lone pairs.



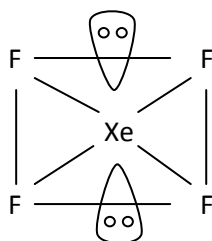
Structure of XeF_5^-

STRUCTURE AND BONDING

Valence bond approach:



Here in the compound XeF_4 the central atom Xe is sp^3d^2 hybridised and contains 3bp and 2lp. So it is an octahedral molecule in which 2 axial positions are occupied by lone pairs so it has originally a square planar skeleton.



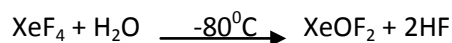
Structure of XeF_4



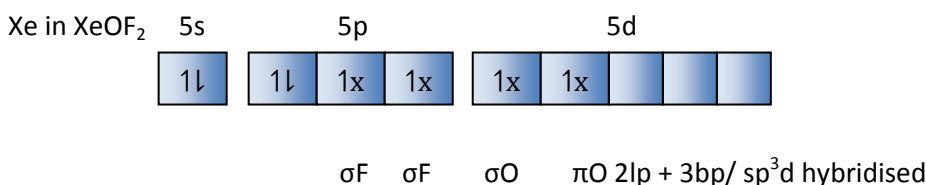
CHEMISTRY OF XENON OXIDE DI-FLUORIDE (XeOF₂)

Preparation:

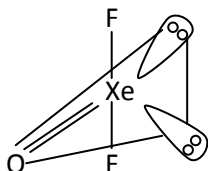
It is prepared by hydrolysis of XeF₄ at -80°C.



Structure and bonding:



Here in the compound XeOF₂, the central Xe atom is sp³d hybridised and contains 2lp and 3bp. So the molecule has trigonal bipyramidal structure in which the two lone pairs and one Xe = O bond occupies the three equatorial position according to Bent's rule.

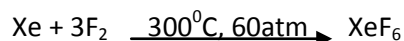


Structure of XeOF₂

CHEMISTRY OF XENON HEXAFLUORIDE (XeF₆)

Preparation:

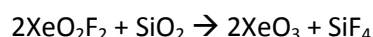
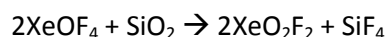
It is best prepared by reacting xenon and fluorine in the ratio 1:20 in a nickel vessel. The reaction is carried out at 300°C and at 60 atm pressure.



Reactions:

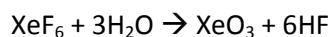
1. **Reaction with glass or quartz vessels:**

It cannot be stored in glass or quartz vessels owing to the following reactions:



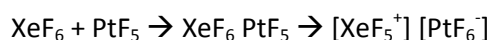
2. **Hydrolysis:**

It reacts with water give xenon trioxide which is highly explosive and makes the handling of XeF_6 extremely difficult.



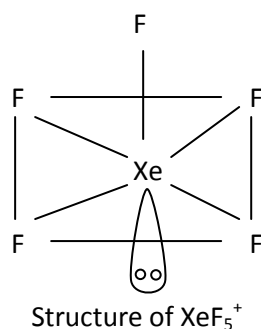
3. **Formation of XeF_5^+ :**

It reacts with fluoride ion acceptors to form the species like XeF_5^+ .



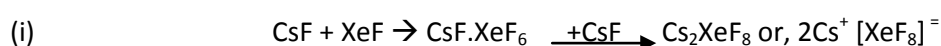
Similar reaction occurs with AsF_5 , SbF_5 and BF_3 .

The XeF_5^+ shows the expected **square pyramidal** structure.



4. **Formation of XeF_8^{2-} species:**

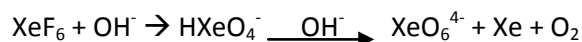
XeF_6 reacts with fluoride ion donors to produce XeF_8^{2-} species as –





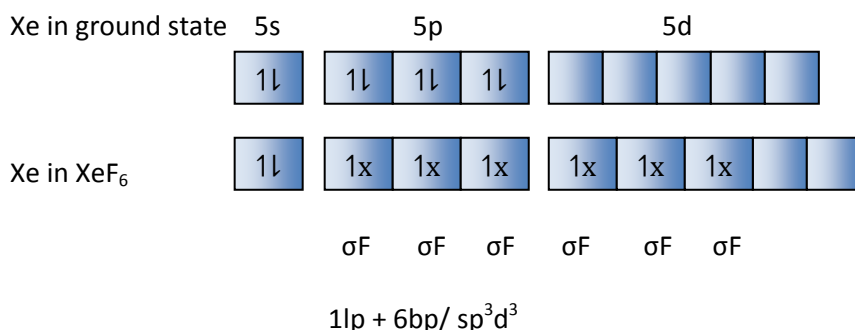
In XeF_8^{2-} , 8bp + 1lp are present and it has a square antiprism structure.

5. **Reaction with base:**

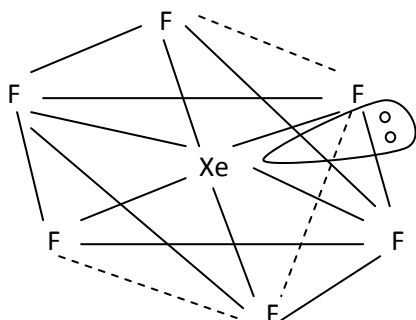


STRUCTURE AND BOND APPROACH

1. **Valence bond approach:**



Here in the compound the central atom Xe is sp^3d^3 hybridised containing one lone pair and 6 bond pairs so the structure is octahedron.



XeF_6 – A FLUXIONAL MOLECULE

In vapour phase XeF_6 exists as a monomeric XeF_6 which has a slightly distorted octahedron structure but the distortion is slightly less than expected from VSEPR. Another important point is the fluxional

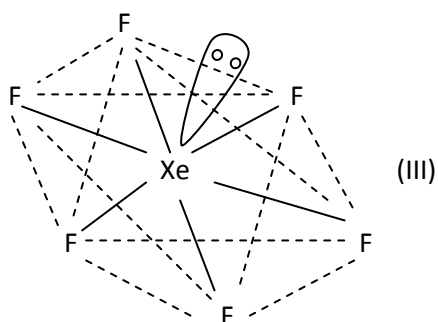
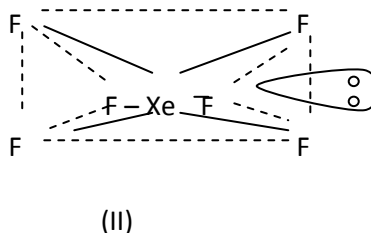
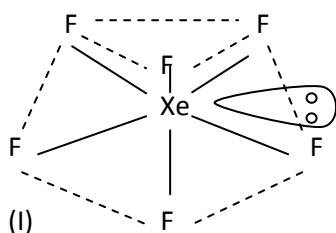


characteristic feature of XeF_6 . If XeF_6 is considered to possess a stereochemistry active lone pair then it has got three possible structures;

(i) Capped trigonal prism (I)

(ii) Pentagonal bipyramidal (II)

(iii) Capped octahedron (III)



Experimentally the molecule is found to be dynamic and fluctuates with time. An intramolecular rearrangement leads to the interchange of the fluorine atoms. This shows the fluxional behaviour i.e. stereochemical non-rigidity of the molecule.

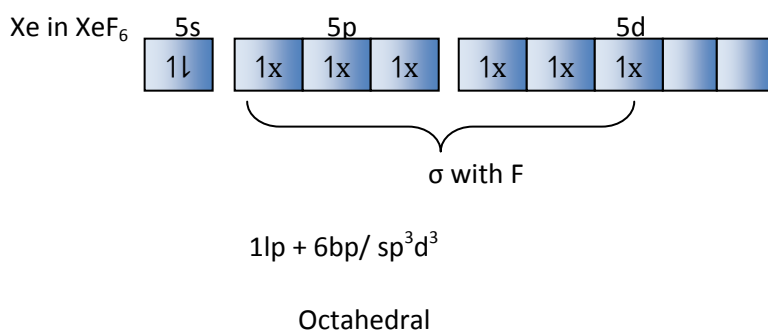
XeF_6 IS DISTORTED OCTAHEDRAL BUT TeCl_6^{2-} IS REGULAR OCTAHEDRAL

Here XeF_6 and TeCl_6^{2-} both are isoelectronic species but their structures are different, XeF_6 is distorted octahedral whereas TeCl_6^{2-} is regular octahedral. This can be explained by considering the nature of the lone pair present in the molecules.

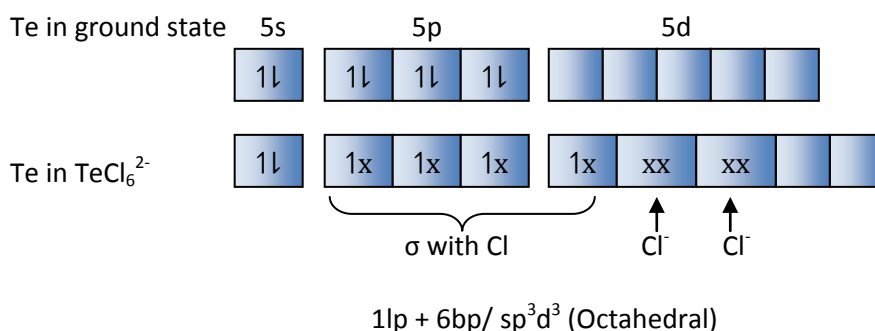
According to the VSEPR theory –

In XeF_6 :





In TeCl₆²⁻:



(i) Stereochemically active lone pairs are those which are involved in determining the shapes of the molecules.

(ii) Stereochemically inactive lone pair never takes part in determination of shapes of the molecules.

Here in TeCl₆²⁻, the central atom Te is very bulky and the ligands Cl⁻ are also very bulky groups in nature so they generate a strong steric strain within the molecule, to minimize this, the lone pair remains in the pure 5s orbital (having no directional sense) and does not come to the surface, this minimizes the steric strain to some extent and the lone pair becomes stereochemically inactive in nature. Thus TeCl₆²⁻ has a regular octahedral shape.

But in XeF₆, due to smaller size of fluorine atoms no such steric strain occurs and lone pair remains in sp³d³ hybridised orbital and stereochemically active in nature.

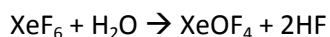
For this reason, XeF₆ is distorted octahedral whereas TeCl₆²⁻ is regular octahedral shape.

CHEMISTRY OF XENON OXIDE TETRAFLUORIDE (XeOF₄)

Preparation:

1. It may be prepared by partial hydrolysis of XeF₆.



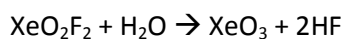
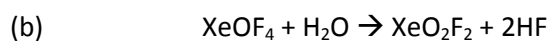
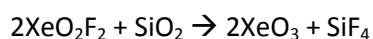
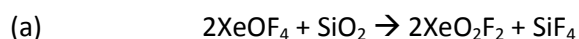


2. It can be prepared by the reaction of SiO_2 with XeF_6 .

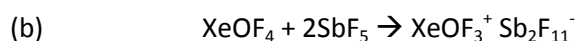


Reactions:

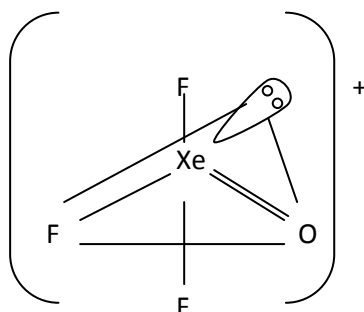
1. **It reacts with SiO_2 and water:**



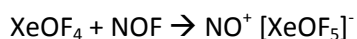
2. **Reaction with F^- acceptors:**



XeOF_3^+ has a TBP structure in which oxygen and lp will remain in equatorial plane in accordance with Bent's rule.;



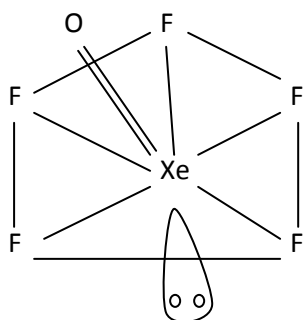
3. **Reaction with F^- donors:**



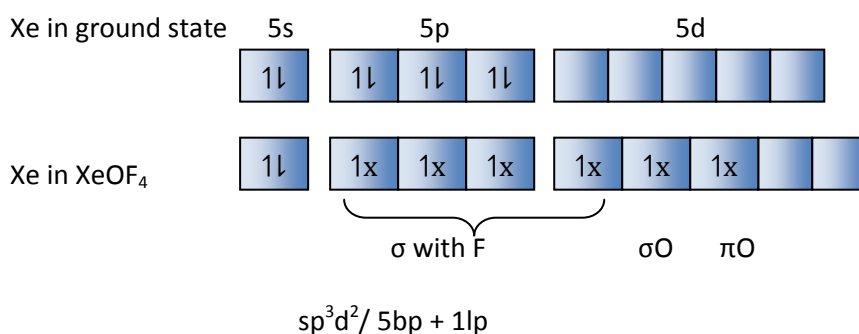
Nitrosyl fluoride

The XeOF_5^- has a pentagonal pyramidal structure with the oxygen in the apical position.

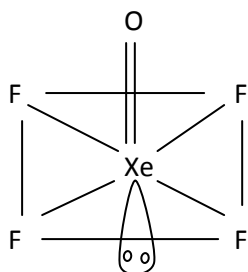




Structure and bonding:



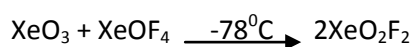
The central atom Xe is sp^3d^2 hybridised containing 1lp and 5bp, so the structure is square pyramidal.



CHEMISTRY OF XENON DIOXIDE DIFLUORIDE (XeO₂F₂)

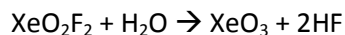
Preparation:

It is prepared by mixing XeO₃ and XeOF₄ at low temperature (-78°C). The product is purified by fractional distillation.

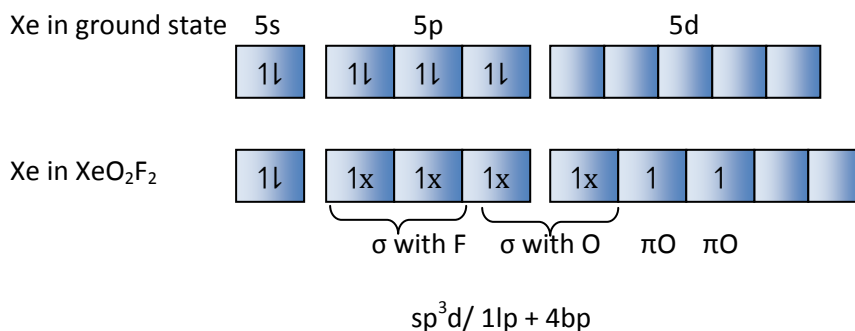


Reactions:

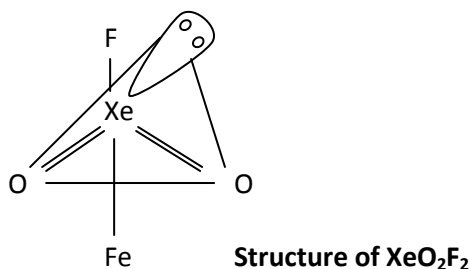
It is easily hydrolysed to give XeO_3



Structure and bonding:



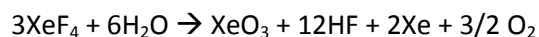
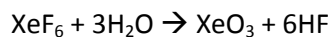
The central atom Xe in XeO_2F_2 is sp^3d hybridised containing 1lp and 4bp so the structure is trigonal bipyramidal and according to Bent's rule two oxygen atoms (π bonded) and lone pair will remain in equatorial plane.



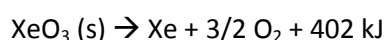
CHEMISTRY OF XENON TRIOXIDE (XeO_3)

Preparation:

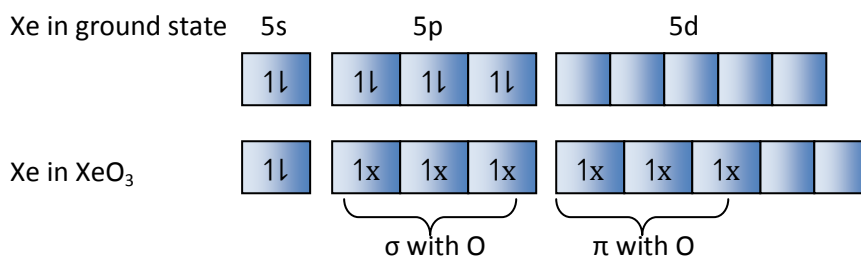
It is prepared by the hydrolysis of XeF_6 and XeF_4 . Great care is to be taken during its preparation as it is highly explosive.



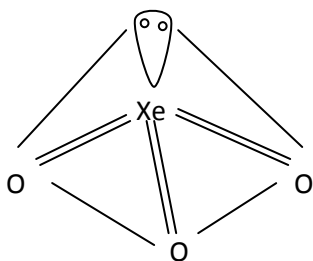
Reactions: It is highly explosive substance.



Structure and bonding



$sp^3 / 1lp + 3bp$ The central atom is sp^3 hybridised containing 1lp and 3bp. So the compound has a tetrahedral structure



CHEMISTRY OF XENON TETROXIDE (XeO₄)

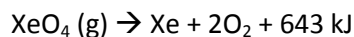
Preparation:

It is prepared by the action of concentrated H₂SO₄ on sodium or barium xenate [Na₄XeO₆, Ba₂XeO₆] at room temperature. It may be purified by vacuum sublimation at -78^oC.



Properties:

It is quite unstable and decomposes to xenon and oxygen. It is very explosive and explode even at -40^oC as:



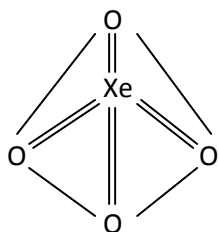
Structure:

sp^3 hybridised containing 0lp + 4bp, tetrahedral.

Now Think:

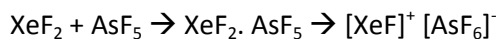
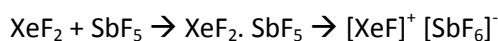
“If you have a goal, write it down. If you do not write it down, you do not have a goal - you have a wish.”





Q. Give one example to show that XeF₂ behaves as a F ion donor.

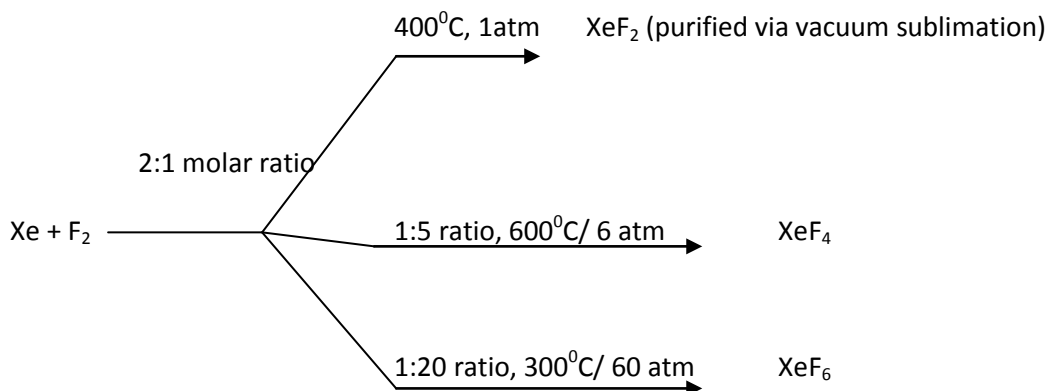
Ans: XeF₂ reacts with SbF₅ or AsF₅ to give the solid compound in which it reacts as a fluoride ion donor.



Q. Write a short note on Xenon fluorides (Preparation, reactions and structure and bonding).

Xenon is an element of noble gas series but it forms a number of compounds with highly electronegative fluorine atom as XeF₂, XeF₄ and XeF₆.

Preparation:

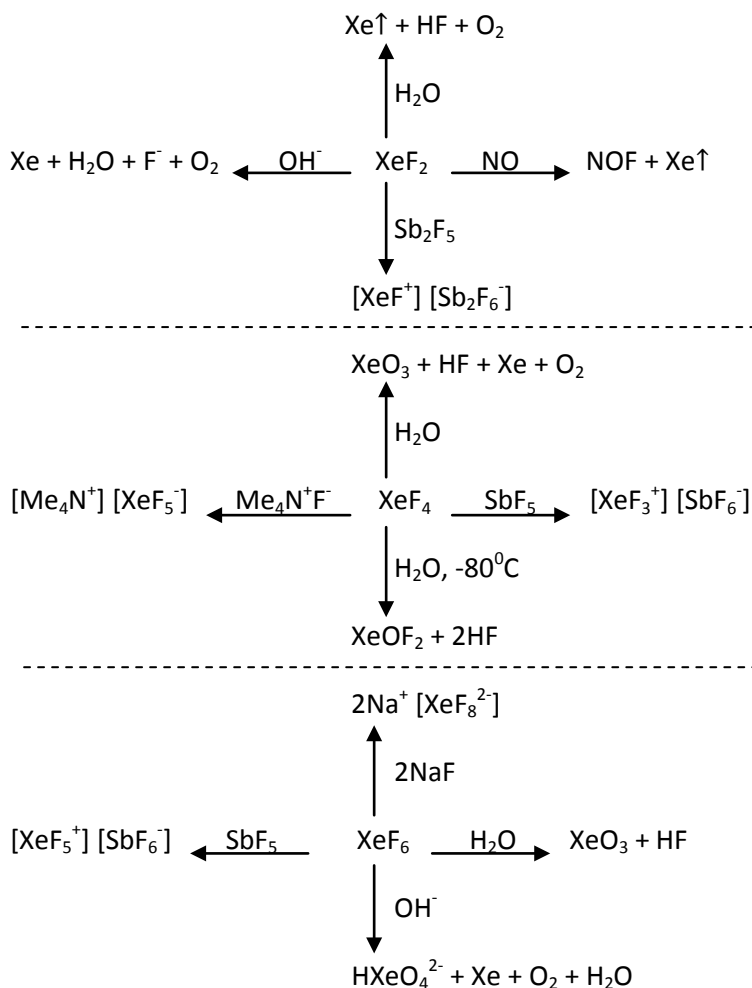


Now Think:

“How would your life be different if...You stopped worrying about things you can't control and started focusing on the things you can? Let today be the day...You free yourself from fruitless worry, seize the day and take effective action on things you can change.”

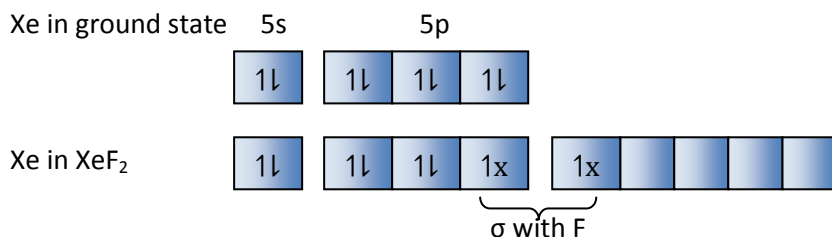


Reactions:

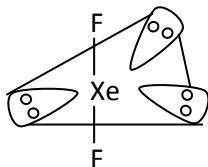


Structure and Bonding:

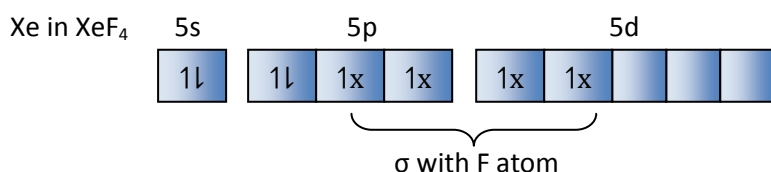
XeF₂:



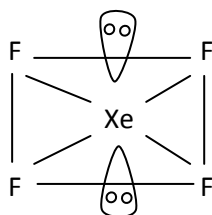
Here central atom Xe contains 3lp + 2bp system and sp^3d hybridised thus it has an ideal TBP structure but according to Bent's rule lone pairs are in the equatorial position thus actual structure becomes linear.



XeF₄:

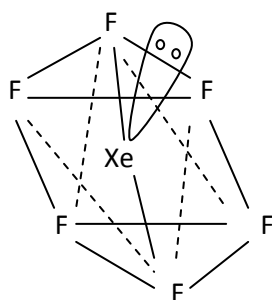


Here central atom is sp^3d^2 hybridised containing 2lp + 4bp system. So the system has an ideal octahedral structure where two axial positions are occupied by lone pair thus it has actually square planar structure.



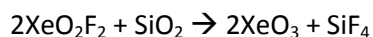
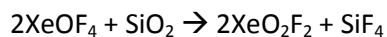
XeF₆:

Central atom Xe is sp^3d^3 hybridised, having 1lp + 6bp system so it has a distorted octahedral structure where distortion is slightly lesser than expected from VSEPR. It is considered that the lone pair is stereochemically active and moves from one face to another face. Due to this reason, XeF₆ also shows fluxionality.



Special Feature:

XeF₆ can't be stored in glass or quartz vessel as it reacts with it to generate highly explosive XeO₃.

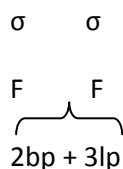
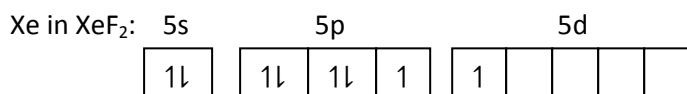
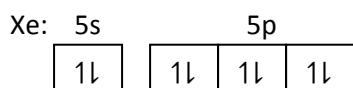


Some other Important questions that came in Calcutta University Exams.

1. XeF₂, XeF₄ and XeF₆ have comparable Xe – F bond energies – Explain.

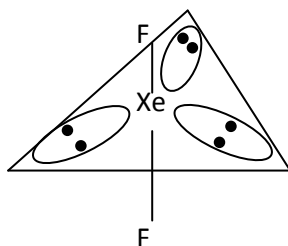
Ans: Structure and bonding of XeF₂ can be explained from two approach (i) V.B approach, (ii) M.O approach.

(i) V.B approach:



Ideal: TBP

Actual: linear



According to Bent's rule, lone pair will remain in equatorial position.



All the xenon fluorides have weak Xe – F bond and weakness of the bond is because of the bond energy factor. Bond energy is also comparable for XeF₂, XeF₄ and XeF₆. This can be explained from M.O approach.

M.O approach for XeF₂:

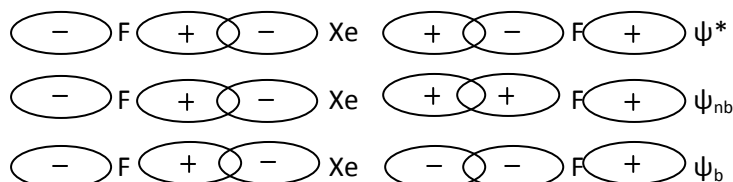


Figure – 1: Interaction between three atomic orbitals in XeF₂

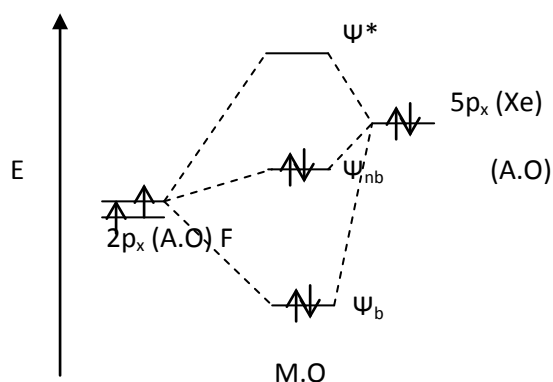


Figure – 2: M.O picture of XeF₂

2p_x orbitals of each fluorine containing the unpaired e⁻ will participate in the formation of 3 centre σ M.O with 5p_x of Xe. The 4e⁻s (1 in each 2p_x of F and 2 in 5p_x of Xe) are now placed in the σ – M.O. These occupy the lowest M.O i.e. bonding and non-bonding. In XeF₂, there atomic orbitals combines to form one bonding, one non bonding and one antibonding M.O. The model can explain the strong U.V absorption at 158 nm due to the transition from non bonding to antibonding M.Os. The distribution of the e⁻s in the σ M.Os concentrate towards the F atoms as both the bonding and nonbonding σ M.Os are placed closer to the atomic orbitals of fluorine, compare to Xe. It develops polarity F^{δ-} - Xe^{δ++} - F^{δ-}. Then in the formation of the compounds 5p e⁻s of Xe are moved towards the 2p_x orbitals of fluorine. In XeF₂, one 3c – 4e bond is present and for each bond, bond order is nearly 0.5.

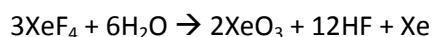
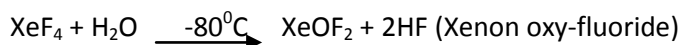
In XeF₄, 5 atomic orbitals combine to produce two bonding, two antibonding and one nonbonding M.O. Similarly, in XeF₆, 7 atomic orbitals combine to give the corresponding M.O. All three Xenon fluorides have 3c – 4e type of bonding, but, number of this type of bond are different XeF₂ has 1 (3c – 4e) bond, XeF₄ has two (3c – 4e) bond and XeF₆ has three (3c – 4e) bond.



It is known that $B.O \propto B.E \propto B.S$. A single bond is spread over the $F - Xe - F$ system which gives a bond order 0.5 for each $Xe - F$ bond. Since, all compounds have $3c - 4e$ type bonding, B.O and B.E also comparable. This also accounts for the existence of weak $Xe - F$ bond in xenon fluorides.

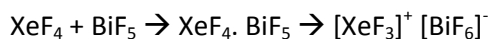
2. Complete the following reaction:

XeF₄ + H₂O → Ans: Xenon tetrafluoride (XeF₄) is readily hydrolysed by water. The reaction can be controlled to yield different products.



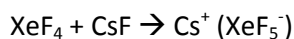
(Xenon trioxide)

3. Write down the product of the following reaction: XeF₄ + BiF₅ → Ans: XeF₄ can act as a fluorinating agent and hence, it will react with the fluoride ion acceptor. BiF₅ is a fluoride ion acceptor. Then, the reaction is



4. Predict the structure of anion formed in the reaction between CsF and XeF₄.

Ans: Alkali metal fluorides MF (NaF, KF, RbF, CsF) act as a fluoride ion donor and the reaction between CsF and XeF₄ is as follows-



The structure XeF₅⁻ can be predicted as pentagonal planar.

Give it a Thought-

- Not to give up under any circumstances should be the motto of our life: we shall try again and again, and we are bound to succeed. There will be obstacles, but we have to defy them. So do not give up, do not give up! Continue, continue! The goal is ahead of you. If you do not give up, you are bound to reach your destined goal."
- "People who lack the clarity, courage, or determination to follow their own dreams will often find ways to discourage yours. When you change for the better, the people around you will be inspired to change also....but only after doing their best to make you stop. Live your truth and don't EVER stop."

