Module IV : Noble Gases

Group 18:

$_{2}He$: $1s^2$

$_{10}Ne$: $1s^2\ 2s^2\ 2p^6$

$_{18}Ar$: $[Ne]\ 3s^2\ 3p^6$

$_{36}Kr$: $[Ar]\ 3d^{10}\ 4s^2\ 4p^6$

$_{54}Xe$: $[Kr]\ 4d^{10}\ 5s^2\ 5p^6$

$_{86}Rn$: $[Xe]\ 4f^{14}\ 5d^{10}\ 6s^2\ 6p^6$

* These are gases, chemically unreactive due to stable configuration.

* They are termed as inert gases and rare gases.

⇒ Occurrence:

* Except Rn, all the noble gas occur in universe in free state.

* Present in Stars and earth's atmosphere.

* Xn, Rn Present in natural gas and in radioactive minerals (pitchblende and monazite).

* Main commercial source of helium is natural gas.

* Radon is radioactive α-decay product of radium.

$$^{226}_{88}Ra \longrightarrow {}^{222}_{86}Rn + {}^{4}_{2}He$$

History of the discovery of noble gases:-

a) Cavendish's experiments:

* During his attempts to determine the composition of air, it was Cavendish who obtained the first experimental evidence for the noble gases in 1785.
* He electrically sparked the purified air which is mixed with excess oxygen in a jar repeatedly in order to make oxygen react with the whole of nitrogen to form nitrogen oxides.

⇓

* The residual gases were then passed first through aqueous KOH to absorb nitrogen oxides and CO_2.

⇓

Then pass through potassium pentasulphide (K_2S_5) to absorb oxygen.

* He found that a very small residual part of air remained as such.

* More than a century later, this unreactive fraction was eventually shown to be a mixture argon & other noble gases.

b) Discovery of helium:-

* A new bright yellow emission line, which matched none of then discovered elements, was first found in the spectrum of the solar corona during solar eclipse in 1868 by Lockyer and Frankland.

* This discovery made them propose the existence of a new element helium.

c) Discovery of argon:-

* In the early 1890s, Lord Rayleigh and William Ramsay independently observed that the apparent density of nitrogen isolated from air was higher than that of nitrogen obtained from the thermal decomposition of ammonium nitrite.

$$NH_4NO_2 \longrightarrow N_2 + 2H_2O$$

* They cooperatively continued their investigation to find a reason for the discrepancy.
* This led to the isolation and characterization of a new element that was present along with nitrogen isolated from air.
* That unknown gas might fit in to the periodic table after the element chlorine, named argon. (argos; inert, lazy)

d) Discovery of neon, krypton & xenon:

* Rayleigh and Ramsay themselves doubted the presence of more elements in the argon sample.
* They isolated 3 additional elements by low temp evaporation of argon obtained by the fractional distillation of liquid air.
* These elements gave independent spectral lines.

e) Discovery of radon:

* Discovered by Dorn
* α- decay product of radium.

$$^{226}_{88}Ra \longrightarrow {}^{222}_{86}Rn + {}^{4}_{2}He$$

Isolation (separation) of individual Noble gases

1) Isolation of noble gas mixture from air
2) separation of the components of the noble gas mixture.

Step 1 :⇒

Isolation of noble gas mixture from dry air
- Rayleigh and Ramsay's second method (chemical method)

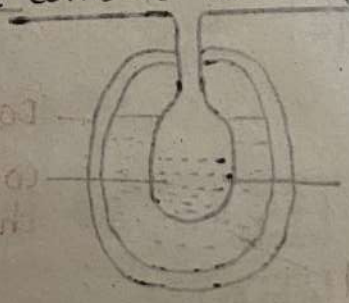
Apparatus consists ⇒

50 L round bottomed flask with

i) two heavy Pt electrodes
ii) a gas inlet tube
iii) an inlet tube for NaOH solution.
iv) outlet tube for used NaOH solution.

1) CO_2 free dry air with dry oxygen (4:1 ratio) is passed into the flask.
2) electric discharge of 6000 to 8000 volt is passed through electrodes. N_2 & O_2 in air combine to form oxides of nitrogen.

$$N_2 + O_2 \longrightarrow 2NO$$
$$2NO + O_2 \longrightarrow 2NO_2$$



3) NaOH solution introduced to absorb nitrogen oxides.

$$2NO_2 + 2NaOH \longrightarrow NaNO_2 + NaNO_3 + H_2O$$

4) The used up NaOH taken out

⇒

* The residual gas in the flask is now a mixture of noble gases & traces of O_2.

5) It passed through alkaline pyrogallol it absorbs O_2.

Step 2 :⇒

Separation of the components of the noble gas mixture - Dewar's method or charcoal adsorption method (physical method)

- It is based on their adsorption on charcoal at different temperature.

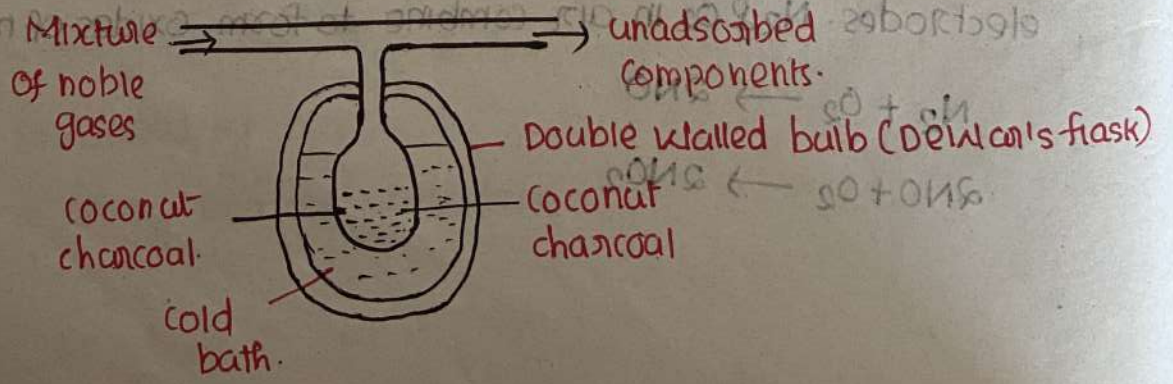


Figure 4.3 ⇒

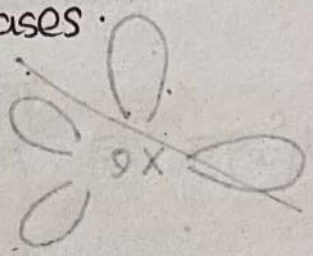
compounds of Noble gases.

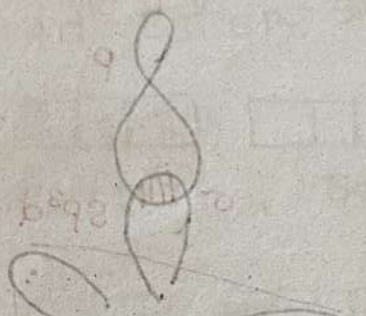
$Xe^{+}[PtF_6]^{-}$

KrF_2

HArF

RnF_2





A) Xenon fluorides

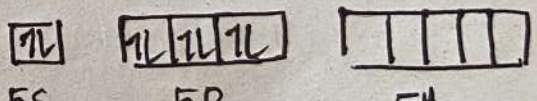
1. XeF_2

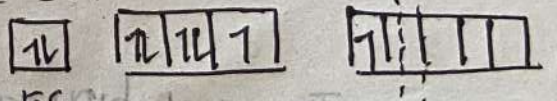
Structure:-

$_{54}Xe$ - $[Kr]\ 4d^{10}\ 5s^2\ 5p^6$ ground state.

$\Rightarrow [Kr]\ 4d^{10}\ 5s^2\ 5p_x^2\ 5p_y^2\ 5p_z^2$

$_{54}Xe$ - $[Kr]\ 4d^{10}\ 5s^2\ 5p_x^2\ 5p_y^2\ 5p_z^1\ 5d^1$ excited state

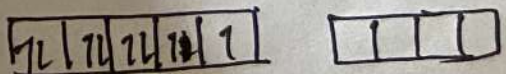
Xe (Ground state) - $[Kr]\ 4d^{10}$ 

Xe (Excited state) - $[Kr]\ 4d^{10}$ 

sp^3d hybridization.

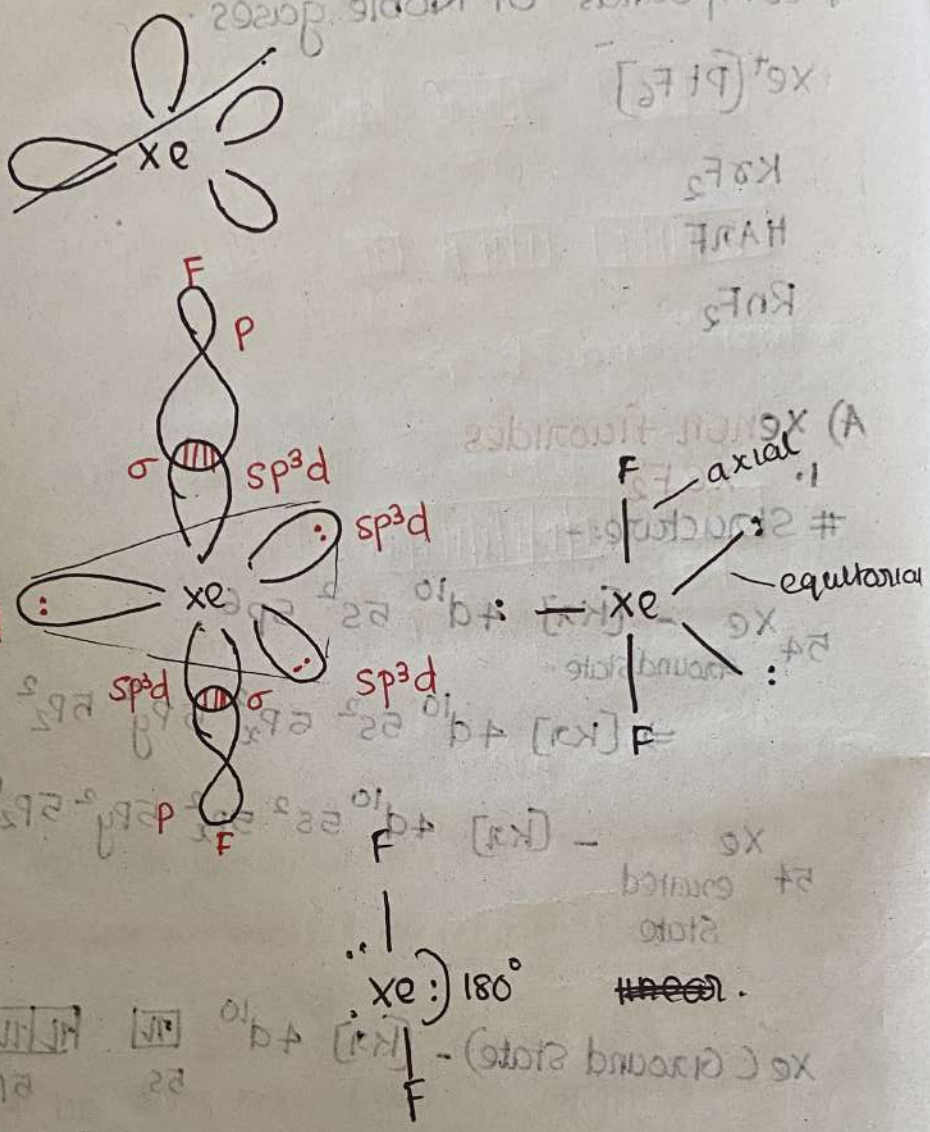
Xe (sp^3d hybridized state):

$[Kr]\ 4d^{10}$ 



sp^3d

→ trigonal bipyramidal



Trigonal bipyramidal - electron pair geometry.

linear - molecular geometry.

2. XeF_4 (xenon tetrafluoride)

Xe Ground State $= [Kr]\ 4d^{10}\ 5s^2\ 5p_x^2\ 5p_y^2\ 5p_z^2$

Xe Excited State $= [Kr]\ 4d^{10}\ 5s^2\ 5p_x^2\ 5p_y^1\ 5p_z^1\ \cancel{5p_z}\ 5d^2$

$Xe_{(G.S)}$: $[Kr]\ 4d^{10}$ | ↿⇂ | ↿⇂ ↿ ↿ | | $5s^2\ 5p_x\ 5p_y\ 5p_z$ $\quad$ $5d$

$Xe_{(E.S)}$: $[Kr]\ 4d^{10}$ | ↿⇂ | ↿⇂ 1 1 | 1 1 | | | | |

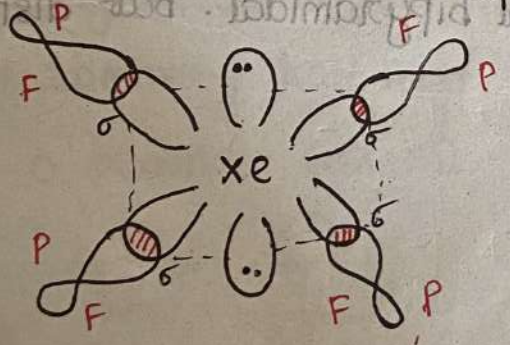
5s — 5p — — 5d

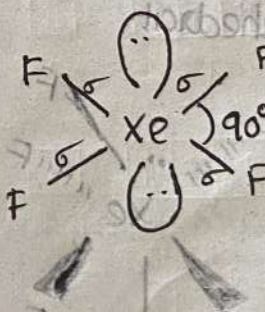
sp^3d^2

Xe (sp^3d^2 hybridized State) :

$[Kr]\ 4d^{10}$ | ↿⇂ ↿⇂ 1 1 1 1 | | | |

sp^3d^2





Squareplanar – molecular geometry.

Octahedral – electron pair geometry.

3) XeF_6 (xenon hexafluoride)

Xe (G.S) : $[Kr]\ 4d^{10}$ | ↑↓ (5s) | ↑↓ ↑↓ ↑↓ (5p) | | | | | (5d)

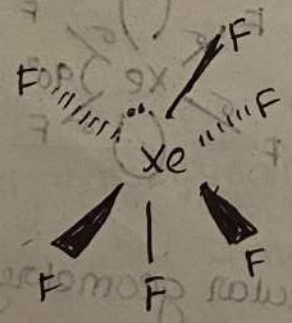
Xe* (E.S) : $[Kr]\ 4d^{10}$ | ↑ (5s) | ↑ ↑ ↑ (5p) | ↑ | ↑ | ↑ | ↑ | ↑ (5d)

sp^3d^3 hybridization.

Xe (sp^3d^3 hybridized state):

$[Kr]\ 4d^{10}$ | ↑↓ ↑ ↑ ↑ ↑ ↑ ↑ (sp^3d^3 hybrid orbitals) | ↑ (5d)

* 6 half filled sp^3d^3 of Xe overlap with half filled 2p orbital of F.
* expect pentagonal bipyramidal. but distorted octahedral.



Distorted o.h geometry

B) Xenon oxides.

1. XeO_3 (xenon trioxide)

Xe (G.S) : $[Kr]\ 4d^{10}$ | 5s | 5P | 5d

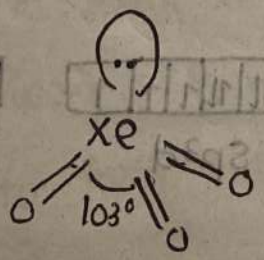
Xe (E.S) : $[Kr]\ 4d^{10}$ | 5s | 5P | 5d

Sp^3 hybridization.

Xe (sp^3 hybridized state) : $[Kr]\ 4d^{10}$ | Sp^3

O : $1s^2\ 2s^2\ 2p_x^2\ 2p_y^1\ 2p_z^1$

* 3 half filled sp^3 overlap with 3 2P orbital of O.
* 3 unhybridized 5d orbital overlap sideways fashion with remaining half filled 2P orbital of oxygen form Xe-O pi bonds. ($d\pi$-$p\pi$)



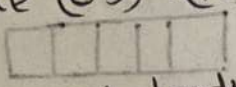
Pyramidal shape.

* angle 103° < tetrahedral angle (109.5°). bcz lonepair exerts greater repulsion on bond pairs.

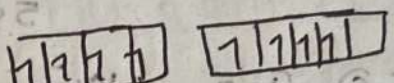
2) XeO_4 (xenon tetroxide)

Xe (G.S) : [Kr] $4d^{10}$ $5s^2$ $5p^6$ $5d$

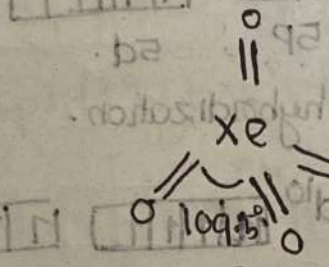
Xe (E.S) : [Kr] $4d^{10}$ $5s^1$ $5p^3$ $5d^4$



Xe (sp^3 hybridized state) : [Kr] $4d^{10}$



sp^3



Pyramidal.

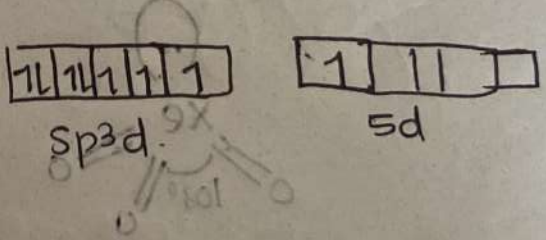
c) xenon oxofluorides (oxy fluorides)

1) $XeOF_2$ (xenon oxo difluoride)

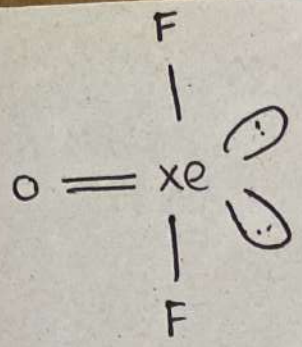
Xe (E.S) : [Kr] $4d^{10}$ $5s^2$ $5p^4$ $5d^2$

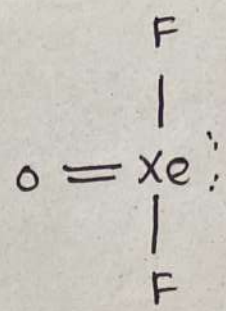
Xe (sp^3d hybridized state)

[Kr] $4d^{10}$



sp^3d $\quad$ $5d$





T-shaped.

O-Xe-F angle $< 90°$ due to greater magnitude of repulsion caused by lone pairs.

2) $XeOF_4$ (xenon oxotetrafluoride).

Xe (G.S) : $[Kr]\ 4d^{10}$ | 5s | 5p | 5d |

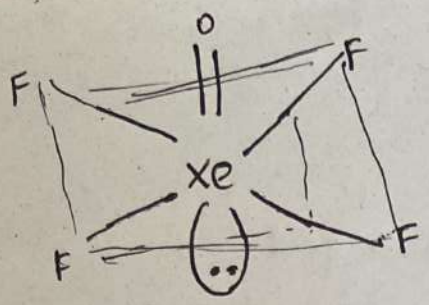
Xe (E.S) : $[Kr]\ 4d^{10}$ | 5s | | | | sp^3d^2 |

O: $1s^2\ 2s^2\ 2p_x^2\ 2p_y^1\ 2p_z^1$

4 sp^3d^2 head on fashion with half filled 2p orbital of F atom to form Xe-F σ bond.

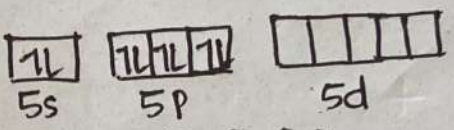
1 sp^3d^2 head on fashion with half-filled 2p orbital of O atom to form Xe-O σ bond.

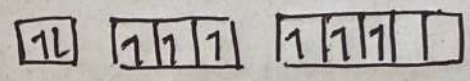
half filled unhybridized 5d of Xe side-ways overlap with half-filled 2p orbital of O atom to form $d\pi$-$p\pi$ bond.



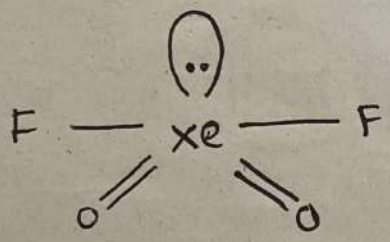
Square pyramidal.

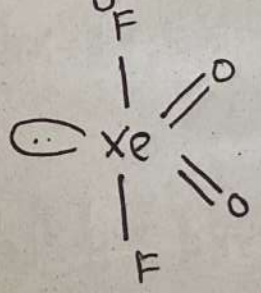
3) XeO_2F_2 (xenon dioxodifluoride)

Xe (G.S) : [Kr] $4d^{10}$ 

Xe (E.S) : Kr $4d^{10}$ 

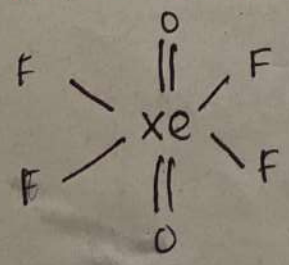
Sp3d hybrid orbital.





See-saw

4) XeO_2F_4 (xenon dioxotetra fluoride)

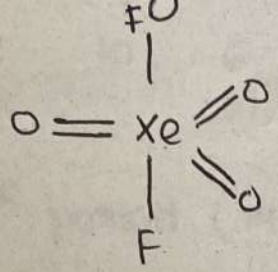


octahedral

Sp^3d^2

5) XeO_3F_2

sp^3d hybridization.



Trigonal bipyramidal

Rxn of xenon fluorides with H_2O

a) $2XeF_2 + 2H_2O \longrightarrow 2Xe + 4HF + O_2$.

b) $6XeF_4 + 12H_2O \longrightarrow 4Xe + 2XeO_3 + 24HF + 3O_2$.

at very low temp like $-80^\circ C$

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

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

$XeF_6 + H_2O \longrightarrow XeOF_4 + 2HF$

$\downarrow H_2O$

$XeO_2F_2 + 2HF$