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Section: Senior TOPIC: Group- 18 Date: 18-06-2020 Name of the student::

COMPOUNDS OF XENON: XENON DIFLUORIDE (XeF₂):

PREPARATION:

(i)

 $\begin{array}{l} \text{Xe} + \text{F}_2 \xrightarrow{\text{Ni-Tube or monel metal (alloy of Ni)}} \text{XeF}_2 \\ \text{O} & \text{Volume ratio should be 2 : 1 otherwise other higher fluorides tend to form.} \end{array}$

(ii)
$$Xe + O_2F_2 \xrightarrow{118^{\circ}C} XeF_2 + O_2$$

(iii)
$$Xe + F_2 \xrightarrow{Hg(arc)} XeF_2$$

Recently discovered method: (iv)

K⁺ [AgF₄]⁻ [potassium tetrafluoroargentate (III)] is first prepared and this is reacted with BF₃

$$K^+ [AgF_4]^- \xrightarrow{BF_3} AgF_3$$
 (red solid) + KBF_4
2 AgF_3 + $Xe \longrightarrow 2 AgF_2$ (Brown solid) + XeF_2

PROPERTIES:

- Colorless crystalline solid and sublimes at 298 K. (i)
- Dissolves in water to give a solution with a pungent odour. Much soluble in HF liquid. (ii)
- This is stored in a vessel made up of monel metal which is a alloy of nickel. (iii)
- (iv) **Reaction with H₂:** It reacts with hydrogen gas at 400°C

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

Hydrolysis: (v)

 $2XeF_{_{2}} + 2H_{_{2}}O \longrightarrow 2Xe + 4HF + O_{_{2}}$ (slow)

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 PCI₅.

Hydrolysis is more rapid with alkali.

$$XeF_2 + 2 NaOH \longrightarrow Xe + \frac{1}{2}O_2 + 2NaF + H_2O$$
 (fast)

The reaction (a) is slower probably due to dissolution of XeF₂ in HF.

Oxidising properties: (vi)

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

The standard reduction potential for XeF₂ is measured to be + 2.64 V. Therfore it acts as a strong oxidising agent.

$$2e^{-} + 2H^{+} + XeF_{2} \longrightarrow Xe + 2HF; SRP = + 2.64 V$$

This oxidises halides (except F⁻) to their respective halogens.

$$XeF_2 + 2 HCI \longrightarrow Xe + 2 HF + CI_2$$

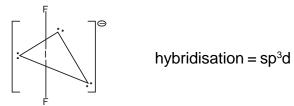
It oxidises $2Br^- \longrightarrow Br_2 + 2e^- \& 2I^- \longrightarrow I_2 + 2e^-$

Similarly it can oxidise BrO₃⁻ (bromate) which are themselves good oxidising agents to BrO₄⁻ 0 (perbromate ions) and Ce+3 to Ce+4 ion.

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

$$C_6H_5I + XeF_2 \longrightarrow C_6H_5IF_2 + Xe$$
; $CH_3I + XeF_2 \longrightarrow CH_3IF_2 + Xe$

O CH_3IF_2 exists as $CH_3^+IF_2^-$, IF_2^- is analogous to I_3^-

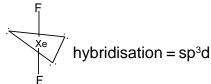


- \mathbf{O} \mathbf{F}_3^- can not be formed as it has no d-orbitals to attain sp³d hybridisation.
- ($\forall iii$) Reactions of XeF₂ + HF (anhydrous) :

$$\begin{array}{c} \operatorname{Pt} + 3\operatorname{XeF}_2 \stackrel{\operatorname{HF}}{\longrightarrow} \operatorname{PtF}_6 + 3\operatorname{Xe} \; ; \qquad \operatorname{S}_8 + 24\operatorname{XeF}_2 \longrightarrow \operatorname{8SF}_6 + 24\operatorname{Xe} \\ 2\operatorname{CrF}_2 + \operatorname{XeF}_2 \longrightarrow \operatorname{2CrF}_3 + \operatorname{Xe} \; ; \quad \operatorname{2MoO}_3 + \operatorname{6XeF}_2 \longrightarrow \operatorname{2MoF}_6 + \operatorname{6Xe} + \operatorname{3O}_2 \\ \operatorname{Mo} \left(\operatorname{CO} \right)_6 + \operatorname{3XeF}_2 \longrightarrow \operatorname{Mo} \operatorname{F}_6 + \operatorname{3Xe} + \operatorname{6CO} \\ 2 \bigcirc + \operatorname{XeF}_2 \stackrel{\operatorname{HF}}{\longrightarrow} \operatorname{2} \bigcirc \stackrel{\operatorname{F}}{\longrightarrow} + \operatorname{Xe} \\ \operatorname{8NH}_3 + \operatorname{3XeF}_2 \longrightarrow \operatorname{N}_2 + \operatorname{6NH}_4 \operatorname{F} + \operatorname{3Xe} \\ \operatorname{2NO}_2 + \operatorname{XeF}_2 \longrightarrow \operatorname{2NO}_2 \operatorname{F} + \operatorname{Xe} \\ \left(\operatorname{nitronium fluoride} \right) \end{array}$$

(ix) **Formation of addition compounds:** XeF₂ reacts with fluoride ion acceptors to form cataionic species and fluoride ion donors to form fluoroanions.

Structure: Shape linear and geometry trigonal bipyramidal.



XENON TETRAFLUORIDE (XeF₄):

PREPARATION:

Xe +
$$2F_2 \xrightarrow{873 \text{ K}, \atop 7 \text{ bar}, \atop \text{Ni-tube}} \text{XeF}_4$$

PROPERTIES:

- (i) It is a colorless crystalline solid and sublimes at 298 K.
- (ii) It undergoes sublimation, soluble in CF₃COOH. It undergoes hydrolysis violently hence no moisture must be present during it's preparation.

- (iii) Reaction with H_2O : 6 XeF₄ + 12 $H_2O \longrightarrow 4$ Xe + 2XeO₃ + 24 HF + 3O₂
- O XeO₃ is white solid and explosive compound (dry), soluble in water (well behaved in water)
- O XeO₃ reacts with NaOH forming sodium xenate

$$XeO_3 + NaOH \longrightarrow Na^+[HXeO_4]^-$$
 (sodium xenate)

O It disproportionates into perxenate ion in basic medium.

$$2 [HXeO_4]^- + 2OH^- \longrightarrow [XeO_6]^{4-} + Xe + O_2 + 2H_2O$$

Xenic acid (H₂XeO₄) is a very weak acid.

(i)
$$[XeO]_6^{4-} \xrightarrow{H^+} XeO_3 + O_2$$
 (ii) $[XeO_6]^{4-} + Mn^{4-} \longrightarrow MnO_4^{-} + XeO_3$ (slow decomposition)

[XeO₆]⁴⁻ is obtainable as Na₄ XeO₆ . 8H₂O (sodium perxenate)

(iv) Oxidising properties of XeF₄:

$$XeF_4 + 2H_2 \longrightarrow Xe + 4HF$$
; $XeF_4 + 2Hg \longrightarrow Xe + 2HgF_2$

(v) Addition reactions: XeF₄ reacts with fluoride ion acceptors to form cataionic species and fluoride ion donors to form fluoroanions.

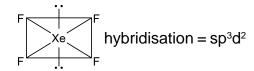
$$XeF_4 + SbF_5 \longrightarrow [XeF_3]^+[SbF_6]^-$$

(vi) Fluorinating agent :

$$XeF_4 + Pt \longrightarrow PtF_4 + Xe$$
; $XeF_4 + 4NO \longrightarrow Xe + 4NOF$ (nitrosyl Fluoride)

$$XeF_4 + 4NO_2 \longrightarrow Xe + 4NO_2F$$
 (nitronium fluoride); $XeF_4 + 2C_6H_6 \longrightarrow C_6H_5F + 2HF + Xe$

Structure: Shape square planar & geometry octahedral



XENON HEXAFLUORIDE (XeF_s):

PREPARATION:

(i)
$$Xe + 3F_2 \xrightarrow{573K,60-70bar} XeF_6$$
 (ii) $XeF_4 + O_2F_2 \longrightarrow XeF_6 + O_2$

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:
 - (a) Complete hydrolysis : $XeF_6 + 3H_2O \longrightarrow XeO_3$ (white solid) + 2HF
 - (b) Partial hydrolysis : $XeF_6 + H_2O \longrightarrow XeOF_4$ (colorless solid) + 2HF
- (v) Reaction with silica (SiO₂):

$$2XeF_6 + SiO_2 \longrightarrow 2XeOF_4 + SiF_4$$

(vi) Thermal decomposition (effect of heat):

$$2XeF_6 \xrightarrow{\Delta} XeF_2 + XeF_4 + 3F_2$$

- O XeF₂ & XeF₄ do not undergo decomposition
- (vii) Formation of addition compounds:

$$\mathsf{XeF}_6^{} + \mathsf{SbF}_5^{} \longrightarrow [\mathsf{XeF}_5^{}]^+ [\mathsf{SbF}_6^{}]^-; \qquad \quad \mathsf{XeF}_6^{} + \mathsf{BF}_3^{} \longrightarrow [\mathsf{XeF}_5^{}]^+ [\mathsf{BF}_4^{}]^-$$

(viii) Reaction With H,:

$$XeF_6 + 3H_2 \longrightarrow 6HF + Xe$$

(ix) Reaction of XeF, with XeO; :

$$XeO_3 + 2 XeF_6 \longrightarrow 3 XeOF_4$$

(x) F⁻ donating/ F⁻ accepting properties: XeF₆ reacts with fluoride ion acceptors to form cataionic species and fluoride ion donors to form fluoroanions.

$$XeF_6 + MF \longrightarrow M^+ [XeF_7]^- (M = Na, K, Rb \text{ or Cs})$$

donation { $XeF_6 + PtF_5 \longrightarrow [XeF_5]^+ [PtF_6]^-$

$$acceptance \begin{cases} CsF & + XeF_6 \longrightarrow CsXeF_7 \\ (alkali\ metal & (caesium\ heptafluoroxenate) \\ fluoride) \\ 2CsXeF_7 \longrightarrow XeF_6 + Cs_2XeF_8 \\ (caesium\ octafluoroxenate) \end{cases}$$

O Order of oxidising power: $XeF_2 > XeF_4 > XeF_6$

XENON-OXYGEN COMPOUNDS:

 $\begin{array}{l} \text{Hydrolysis of XeF}_4 \text{ and XeF}_6 \text{ with water gives XeO}_3. \\ 6 \text{ XeF}_4 + 12 \text{ H}_2\text{O} & \longrightarrow 4 \text{ Xe} + 2 \text{ XeO}_3 + 24 \text{ HF} + 3 \text{ O}_2 \\ \text{XeF}_6 + 3 \text{ H}_2\text{O} & \longrightarrow \text{XeO}_3 + 6 \text{ HF} \\ \text{Partial hydrolysis of XeF}_6 \text{ gives oxyfluorides, XeOF}_4 \text{ and XeO}_2\text{F}_2 \,. \\ \text{XeF}_6 + \text{H}_2\text{O} & \longrightarrow \text{XeOF}_4 + 2 \text{ HF} \\ \text{XeF}_6 + 2 \text{ H}_2\text{O} & \longrightarrow \text{XeO}_2\text{F}_2 + 4 \text{ HF} \end{array}$

XeO₃ is a colourless explosive solid and has a pyramidal molecular structure. XeOF₄ 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 ballons for meterological 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 handing substances that are air—sensitive.

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