

the oxidation number of nitrogen decreases from +5 (in HNO_3) to +2 (in NO) indicating that HNO_3 is being reduced or HNO_3 is acting as an oxidising agent.

10) Balancing oxidation-reduction reactions:

There are two well known methods for balancing oxidation-reduction reactions.

I) Ion-electron method.

II) oxidation number method.

I) Ion-electron method.

Chemical equations describing redox reactions in aqueous solutions are balanced by the ion-electron method. It consists of the following steps: (Reactions in Acidic solution)

1. Split the complete equation into two separate half-reactions, one for the change undergone by the oxidising agent and the other for the change undergone by the reducing agent.

2. Balance each half-reaction not only with regard to the number and kind of atoms but also with respect to the number of positive and negative charges. For this purpose, proceed as under:

(a) use simple multiples before each species so as to balance the number of all atoms except 'H' and 'O'.

(b) Add H_2O to the side deficient in oxygen.

(c) Add H^+ to the side deficient in 'H'.

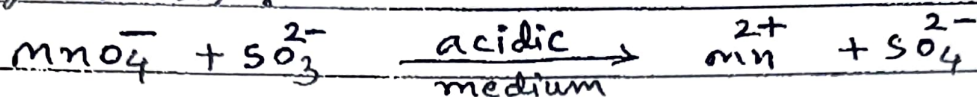
(The solution must be acidic)

(d) Add electrons to the side deficient in electrons.

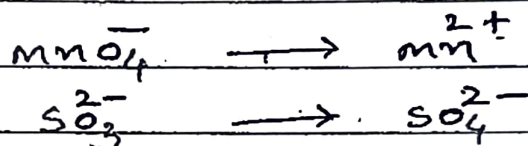
3. multiply one or both half reactions by a suitable numbers so that on adding the two equations, the electrons are balanced.

4. Add the two balanced half reactions.

Example (i): consider the oxidation of sulphite, SO_3^{2-} , into sulphate, SO_4^{2-} ion by acidified potassium permagnate as:

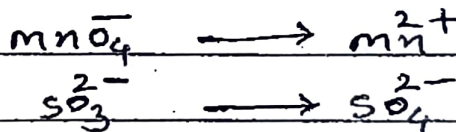


Step.1: Splitting the complete equation into two half reactions.

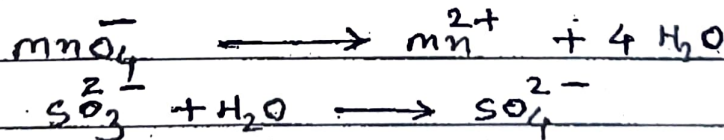


Step.2: Balancing the half reactions

(a) Balancing of all the atoms except H and O

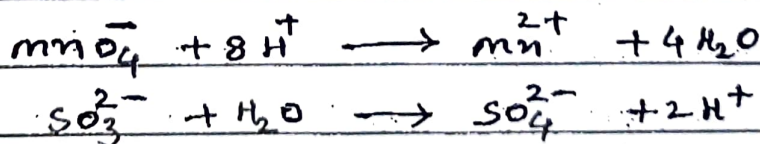


(b) Adding H_2O to the side deficient in oxygen

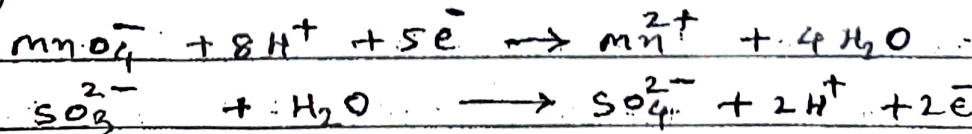


(c) Adding H^+ to side deficient in hydrogen.

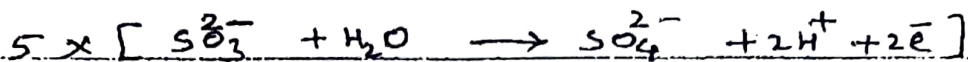
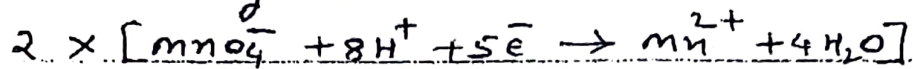
(The solution is acidic as required)



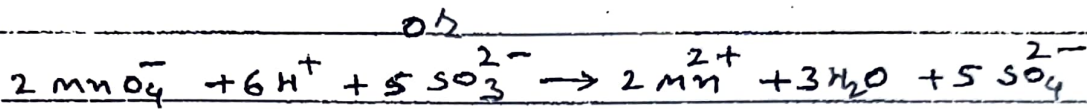
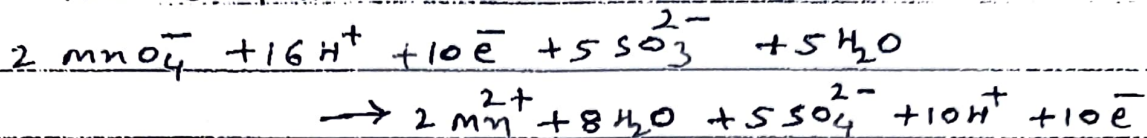
(d) Adding electrons to side deficient in electrons.



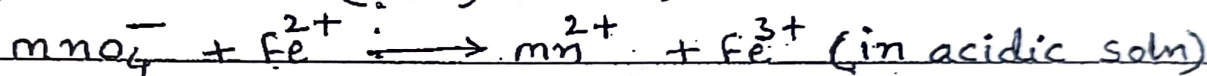
Step 3 : Balancing the electrons



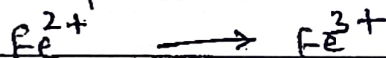
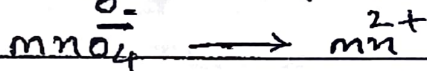
Step 4 : Adding the two balanced half-reactions to get the complete reaction.



Example (ii) Consider the oxidation of ferrous (Fe^{2+}) to ferric (Fe^{3+}) ion as

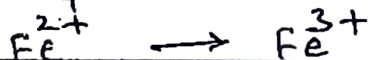
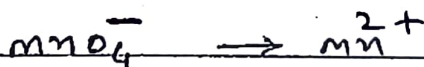


Step-1 : splitting the equation into two half reactions

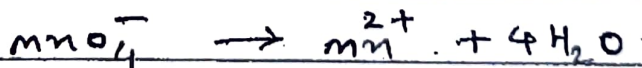


Step-2 : Balancing the two half reactions

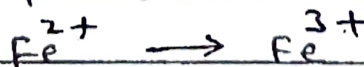
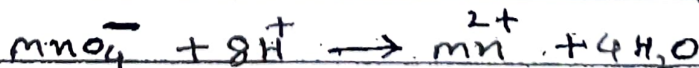
(a) Balancing of all the atoms except 'H' and 'O'



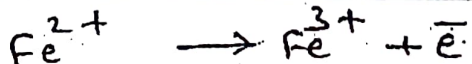
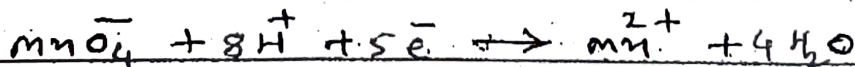
(b) Adding H_2O to the side deficient in oxygen



(c) Adding H^+ to the side deficient in hydrogen

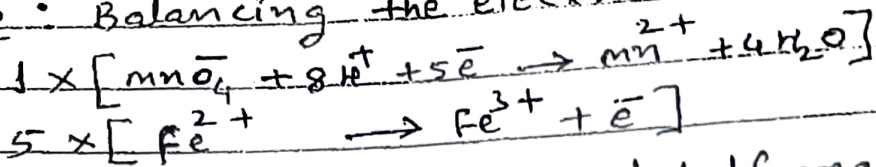


(d) Adding electrons to the side deficient in electrons

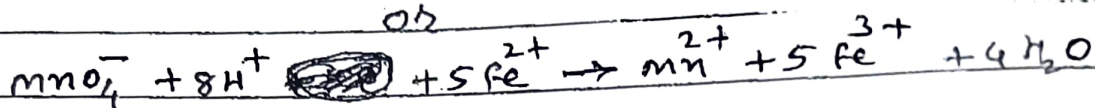
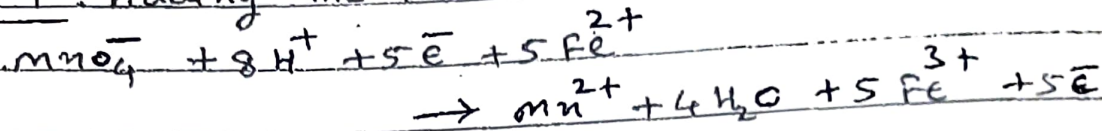


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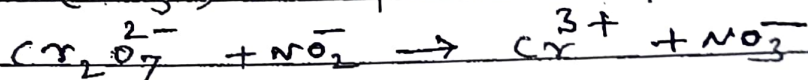
step-3 : Balancing the electrons



step-4 : Adding the two balanced half reactions

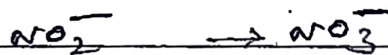
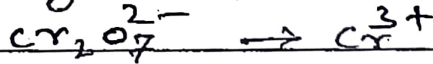


Example (iii) : consider oxidation of nitrite (NO_2^-) to nitrate (NO_3^-) ion by acidified potassium dichromate



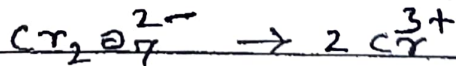
in acidic medium.

step-1 : splitting the equation into two half-reactions

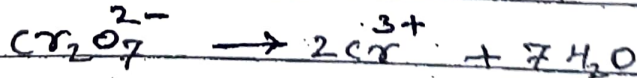


step-2 : Balancing the two half reactions

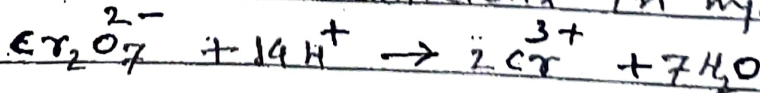
(a) Balancing of all the atoms except H and O



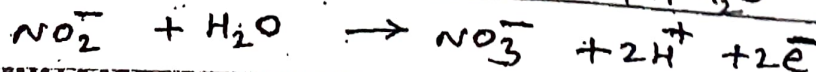
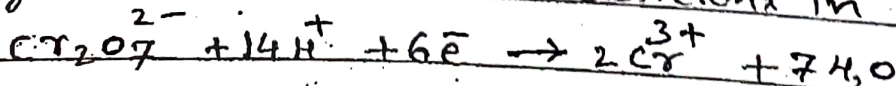
(b) Adding H_2O to the side deficient in oxygen



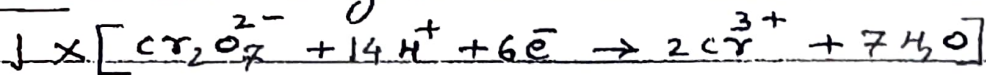
(c) Adding H^+ to the side deficient in hydrogen



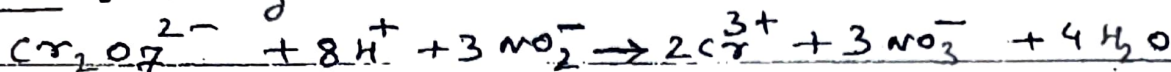
(d) Adding electrons to the side deficient in electrons



step-3: Balancing the electrons.



step-4: Adding the two balanced half-reactions



Example-(iv): Oxidation of ferrous (Fe^{2+}) to ferric (Fe^{3+}) by hypo-iodous acid.

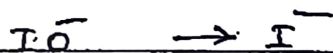


step-1: Splitting the equations into two half reactions.



step-2: Balancing the two half reactions.

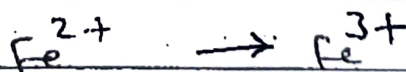
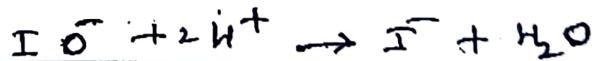
(a) Balancing of all the atoms except H and O.



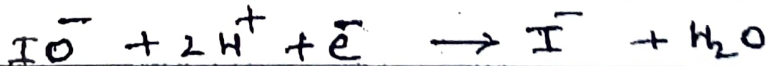
(b) Adding H_2O to the side deficient in oxygen.



(c) Adding H^+ to the side deficient in hydrogen.



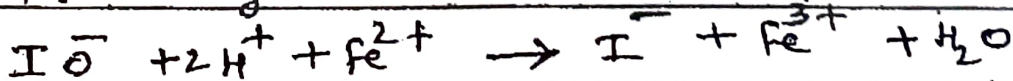
(d) Adding electrons to the side deficient in electron



step-3: Balancing the electrons

The electrons are already balanced.

step-4: Adding the two balanced equations,

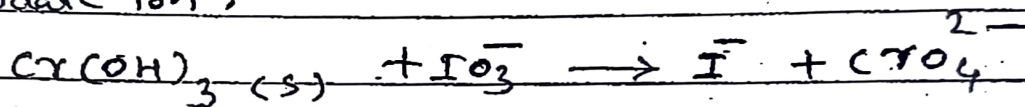


Reactions in Basic solutions :-

If a reaction takes place in an alkaline solution, equations can not contain H^+ ions. Therefore in order to add H atoms in step 2 (C) mentioned before H_2O molecules are added to make up the deficiency of H atoms. At the same time, an equal number of OH^- ions are added to the other side of the equation so that the number of oxygen and hydrogen atoms on both sides is the same.

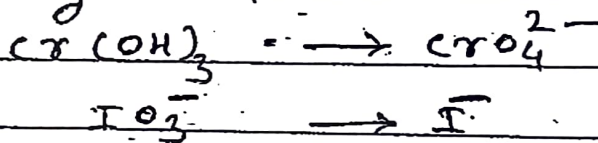
The other steps remain the same.

Example (V) : The reaction between chromic hydroxide and iodate ion :



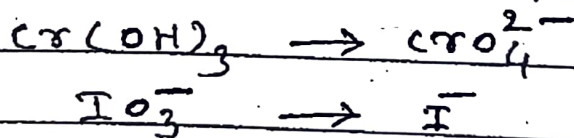
The various steps involved are as follows.

Step - I : Splitting the equation into two half reactions.

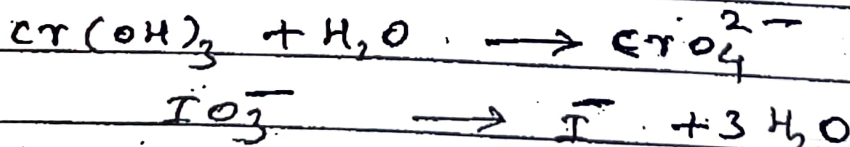


Step - II : Balancing the two half reactions.

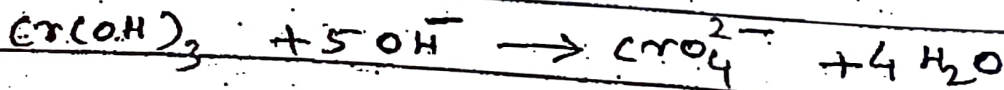
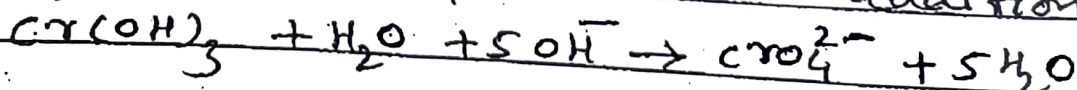
(a) Balancing of all the atoms except H and O

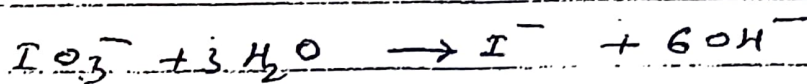
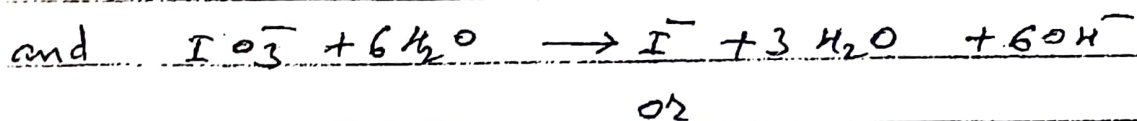


(b) Balancing oxygen by H_2O molecule addition.

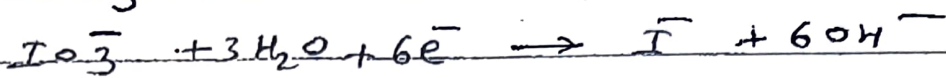
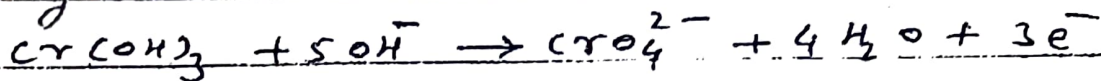


(c) Balancing hydrogen by H_2O and OH^- addition

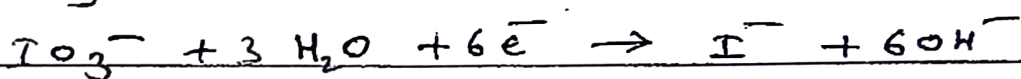
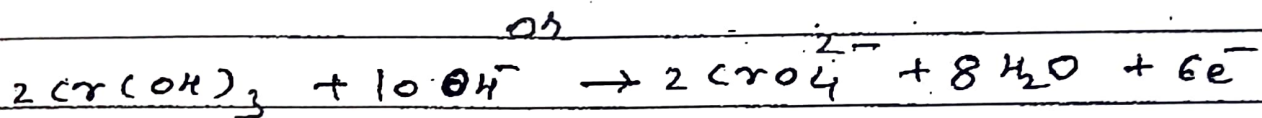
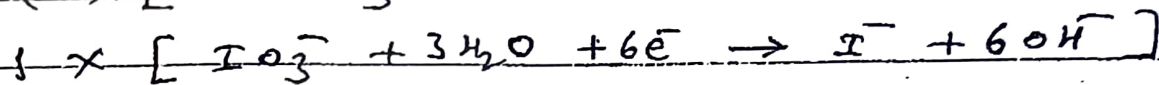
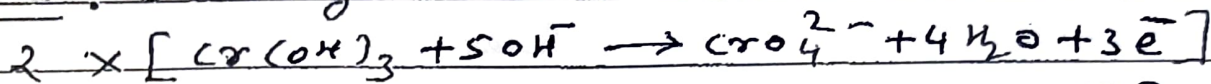




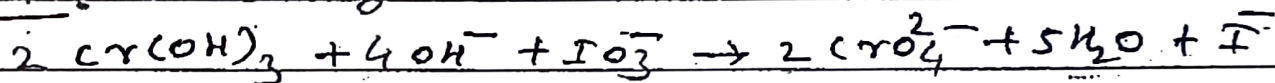
(d) Adding electrons to the side deficient in electron



step-3: Balancing the electrons in both the equations



step-4: on adding the two balanced equations



(II) Oxidation number method for balancing oxidation-reduction equations.

This method is based on the fact that increase in oxidation numbers of one or more atoms must be balanced by a decrease in oxidation numbers of one or more other atoms.

The following steps are employed to balance an oxidation-reduction equation.

step-1: write the oxidation numbers of elements in each compound above the symbol of the element.

step-2: note the element or elements which have undergone change in oxidation number (usually

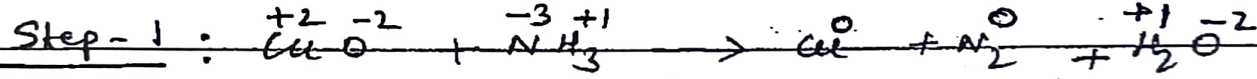
only two elements undergo change), one showing increase in oxidation number (reducing agent) and the other showing decrease in oxidation number (oxidising agent)

Step-3: Balance increase and decrease in oxidation number by choosing proper coefficients for oxidising and reducing agents and the products obtained.

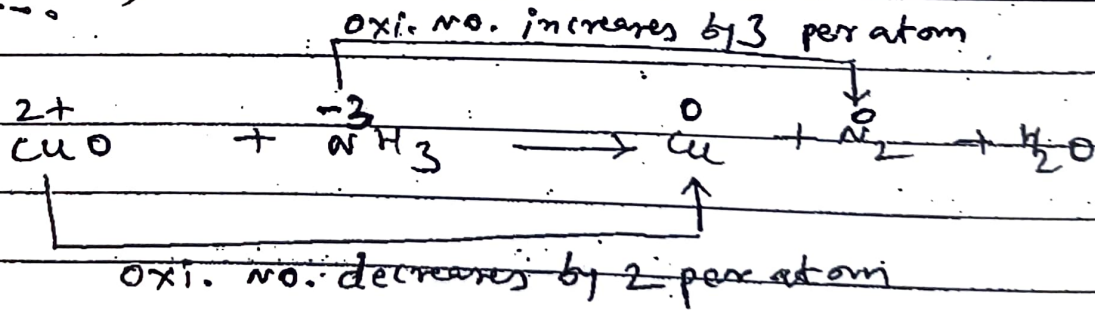
Step-4: Balance hydrogen and oxygen atoms when all other atoms have been balanced.

Example - (i) Reaction between cupric oxide and ammonia.

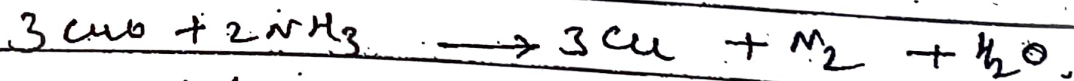
The skeleton equation is :-



Step-2: oxidation no. of copper decreases from +2 to 0, while that of nitrogen increases from -3 to 0; as illustrated below.



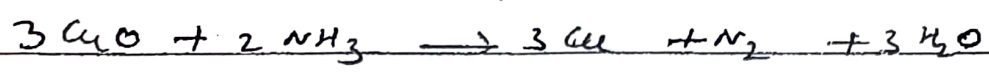
Step-3: Therefore to balance the increase and decrease in oxi. no. multiply CuO by 3 and NH₃ by 2. When we get the equation,



Step-4 → To balance H and 'O' on both sides we

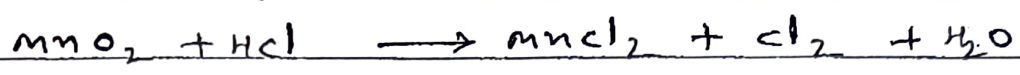
have multiply H_2O by 3 on the right side

Therefore the balanced equation will be,

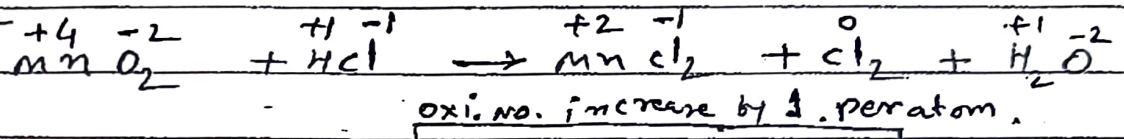


Example: (ii) Reaction between manganese dioxide and hydrochloric acid producing chlorine.

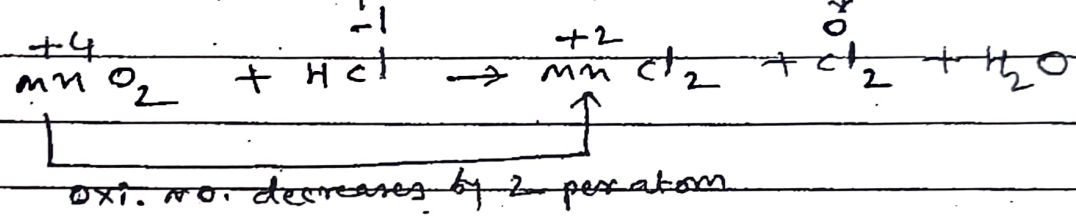
The skeleton equation is



Step - 1

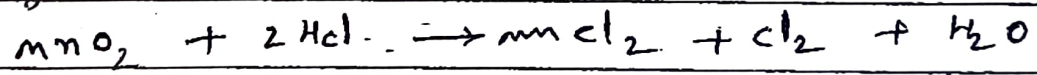


Step - 2



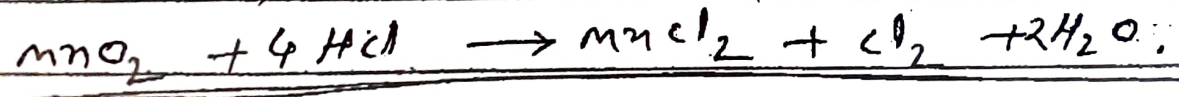
Step - 3 : To balance the increase and decrease in oxi. no. we have to multiply HCl by 2.

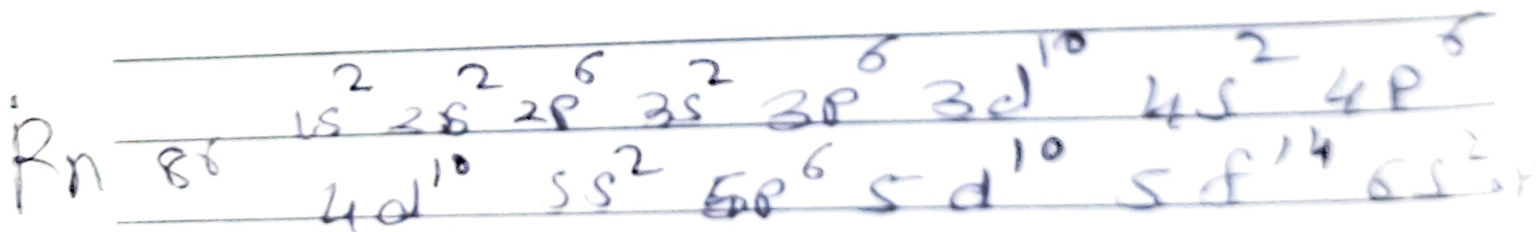
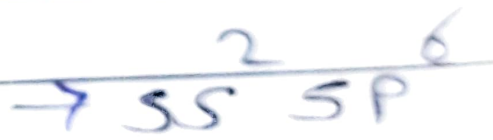
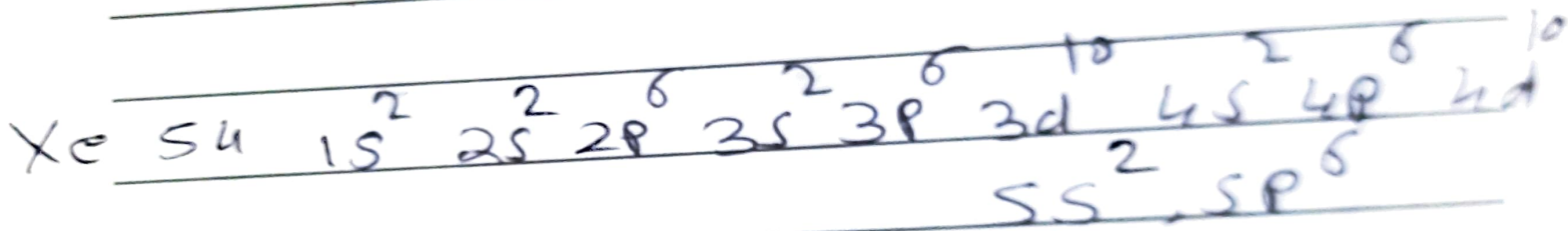
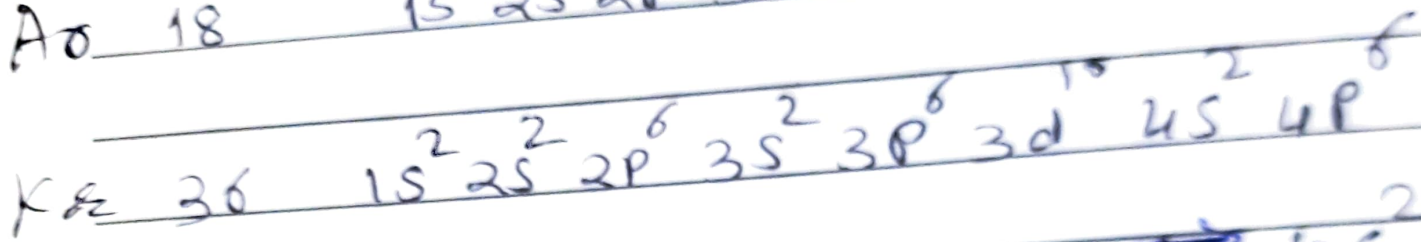
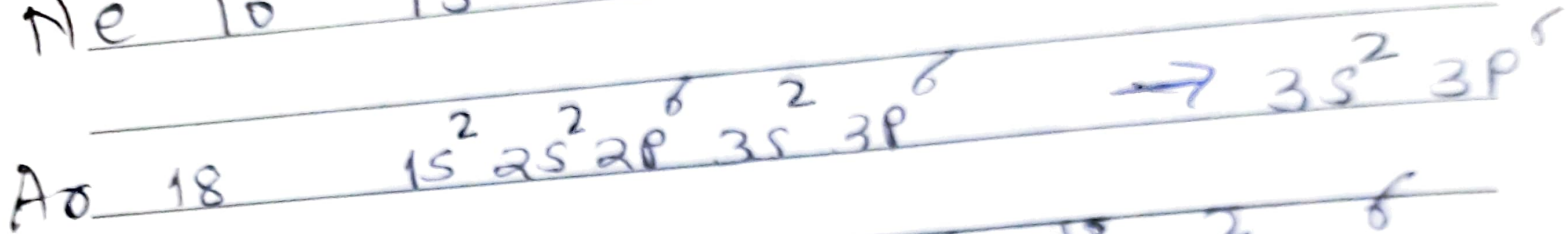
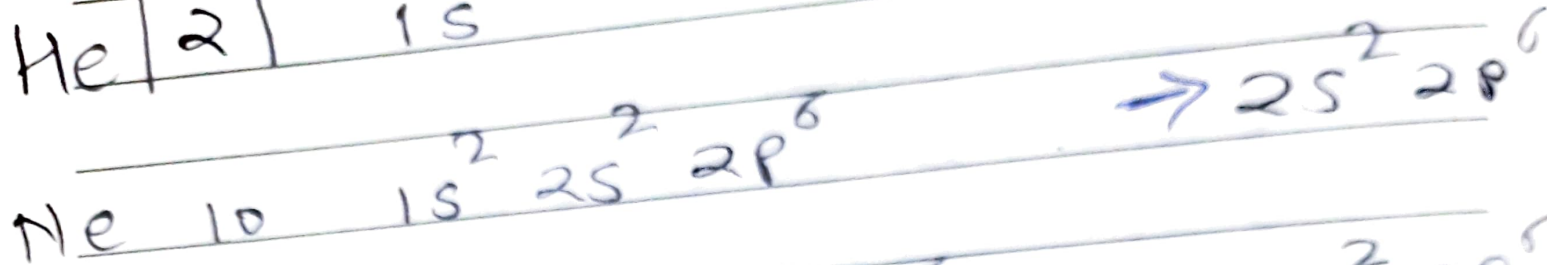
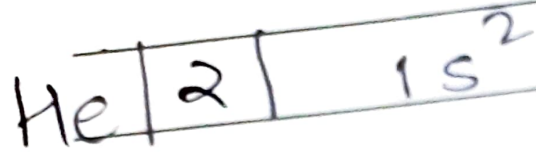
Thus we get.



Step - 4 : Two additional chlorine atoms ^{in $MnCl_2$} are also required. Evidently, these chlorine atoms are not oxidised, because their oxidation number remains the same (-1). i.e. the same as in HCl. These atoms have to be supplied by HCl to balance the equation.

There is also a shortage of one oxygen atoms on right side. After adjusting the coefficient of H_2O to give the same no. of 'H' and 'O' on both sides, the balanced equation will be:—





Introduction :

- 1) Noble gas elements are helium (He) Neon (Ne) Argon (Ar) Krypton (Kr) Xenon (Xe) and Radon (Ra).
- 2) They have very little tendency to form chemical compound with other elements, so they are also called as inert gases.
- 3) But recently researcher have shown that can react with some chemical compound under some specific condition & with some specific element so they are also called as noble gases it shows that they enter into very few chemical reactions.

Position in the periodic table:-

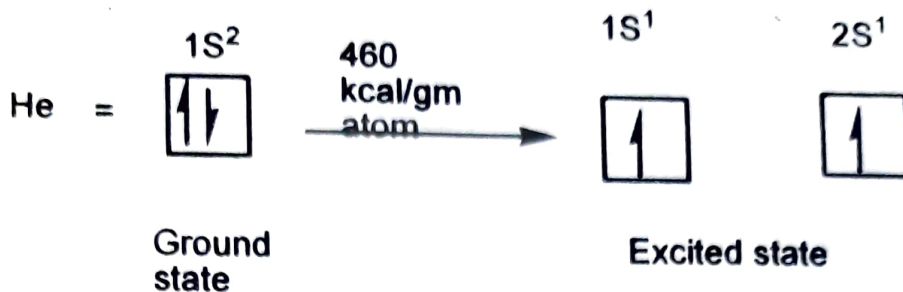
Noble gas elements are placed in P-block and are present in the 18th group and are occupied from 1st period to 6th period they have highly stable $ns^2 np^6$ electronic configuration. Helium has stable $1S^2$ configuration.

The electronic configuration of Noble gas are given below.

Noble gas Element	Outer electronic conf.
${}^2\text{He}$	$1S^2$
${}^{10}\text{Ne}$	$1S^2, 2S^2, 2P^6$
${}^{18}\text{Ar}$	$[\text{Ne}] 3S^2, 3P^6$
${}^{36}\text{Kr}$	$[\text{Ar}] 4S^2, 4P^6$
${}^{54}\text{Xe}$	$[\text{Kr}] 5S^2, 5P^6$
${}^{86}\text{Rn}$	$[\text{Xe}] 6S^2, 6P^6$

A) Under excited condition:-

- 1) If we promote one of the electron from 1S orbital to 2S orbital then condition of chemical activity is expected.



- 2) This require high energy condition ie. 460 Kcal per gram atom and these are influenced electric discharge electron bombardment and radioactivity
- 3) In a discharge tube the helium can form molecule ion, He^+ , and three electron bonded species $(\text{H} \dots \text{He})^+$ and hydrogen Helium combination of the type HeH^+ , HeH_2^+ have be prepared but they survive momentarily.
- 4) Metal electrodes in discharge tube absorb inert gases, to form $\text{Pt}_3 \text{He}$, Fe-He , and Fe-Ar as a intersitial compounds .
- 5) Under suitable conditions of energy halides of a number of elements have been prepared eg. Bi, In, Zn, Na, K, Rb, Pt, Pd, U, I, S etc.

B) Through Co-ordination:-

- 1) Inert gas atoms may donate an electron pair to a powerful electron acceptor.

Booth and Wilson(1935)reported the compounds of argon with born trifluoride

Ar with BF_3 was said to give peaks in the freezing point curves 1Ar:1,2,3,6,8,& 16 BF_3

those in which the gases are trapped in cavities in the crystal frame work of other compounds during their lattice formation.

- 2) H.H.Poweel called these compounds as cage compounds or 'Clatherate compounds' because a molecule of one compound is completely enclosed or trapped by those of the other involving no chemical bonds formation.
- 3) If quinnol (1,4 dihydroxy benzene) is crystallized in the presence of Ar, Kr, or Xe under a pressure of 10-40 atm the gas becomes trapped in the cavities of about 4\AA diameter in the β -quinnol structure.
- 4) They escapes only when the clatherate is dissolved. The compound has approximate composition $(\text{C}_6\text{H}_6\text{O}_2)_3\text{Ar}$.
- 5) However enclatheration does not take place in the case of He or Ne because of small size of He and Ne, the trapping in the cage is not possible.

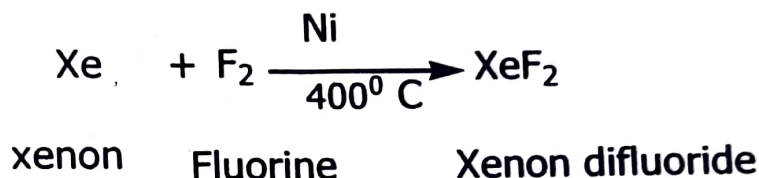
Fluorides of xenon :

Preparation properties & structure of $\text{XeF}_2, \text{XeF}_4, \text{XeF}_6$

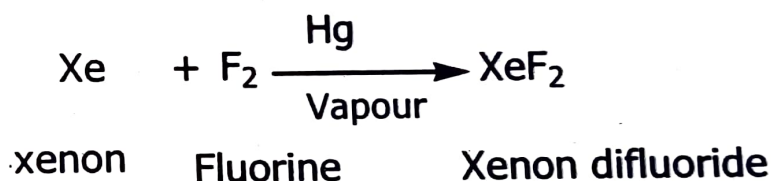
1) XeF_2 (Xenon difluoride):

Preparation :-

- a) Xenon difluoride is best prepared by heating a mixture of xenon and fluorine in 2:1 ratio at 400°C in a sealed nickel tube. On Cooling the above reaction mass colourless solid XeF_2 results.



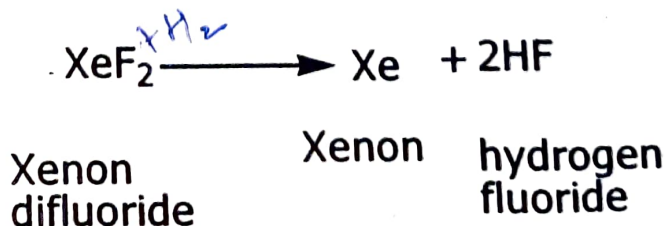
- b) It is also prepared by photochemical combination of xenon & fluorine under the influence of mercury vapour.



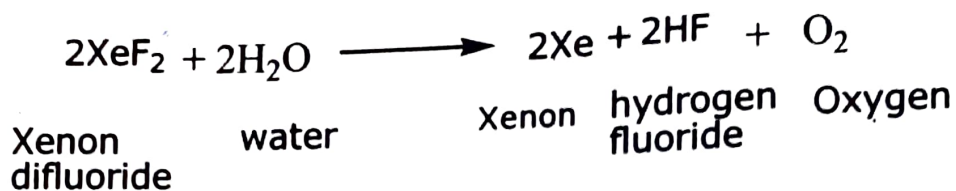
- c) It can also be prepared by fluorination of xenon by oxygendifluoride (O_2F_2) at -178°C

Properties:

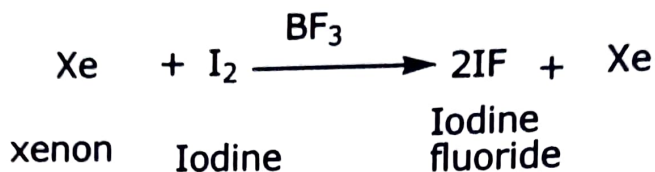
- 1) Xenon difluoride is a colourless crystalline solid which have m.p. 140°C
- 2) It is soluble in HF without reacting
- 3) It reacts with hydrogen to give xenon and hydrogen fluoride.



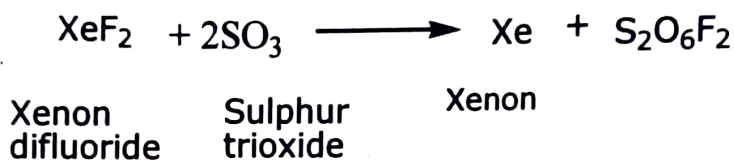
- 4) It reacts with water to give oxygen



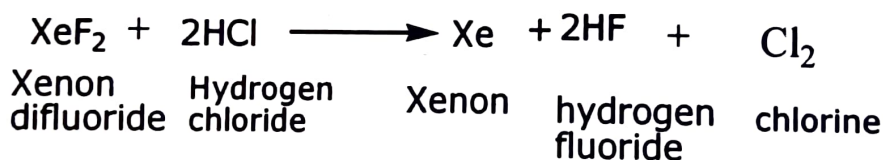
- 5) It oxidizes iodine in the presence of BF_3 to give iodine fluoride (IF)



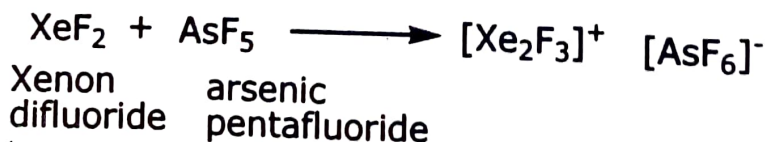
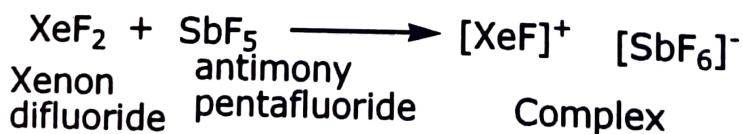
- 6) It reacts with sulphur trioxide to give xenon



- 7) It is mild fluorinating agent i.e. when it reacts with benzene to give fluorobenzene $\text{C}_6\text{H}_5\text{-F}$
- 8) It is strong oxidizing agent it oxidizes HCl to Cl_2 and Ce(III) to Ce(IV) .

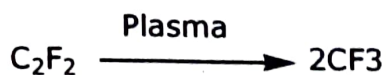


- 9) • In BF_3 solution XeF_2 form complex compound



- 10) It reacts with anhydrous HSO_3F , HClO_4 , CF_3COOH to give mixed fluoro-oxy-compound i.e. FXeSO_2F , $\text{FXeOCIO}_3\text{F}$, FXeO_2CF_3 ,

- 11) It reacts with CF_3 in vapour phase to give $\text{Xe}(\text{CF}_3)_2$ which contain Xe-C bond.



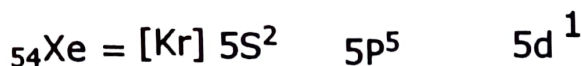
- 12) It reacts with $\text{HN}(\text{SO}_2\text{F})_2$ in CF_2Cl_2



Structure of XeF_2 :



Ground state configuration



Excited state configuration



SP³d-hybridisation

configuration in XeF_2 State

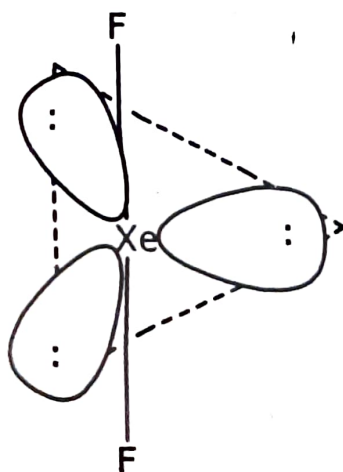


Fig. Linear geometry
SP³d-hybridisation

In the formation of XeF_2 molecule one of the 5P electron shifted to 5d orbital

So one 5S, three P and one 5d orbital hybridise to give sp^3d hybrid orbital containing single electron overlap with half-filled p-orbital to form two Xe-F sigma bond.

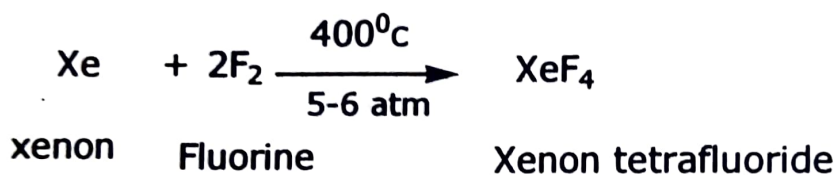
Xenon & Fluorine occupy linear position.

While three equatorial positions are occupied by three lone pairs of e- to minimize electron pair repulsion.

Xenon tetrafluoride [XeF_4]

Preparation:

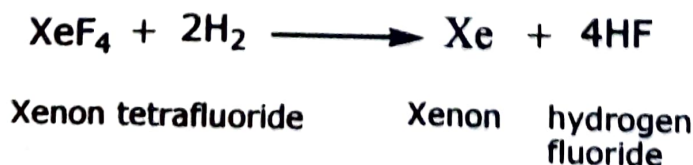
- 1) It is prepared by passing a mixture of xenon & fluorine, in 1:5 ratio through a nickel tube at 400°C under a pressure of 5-6 atm.



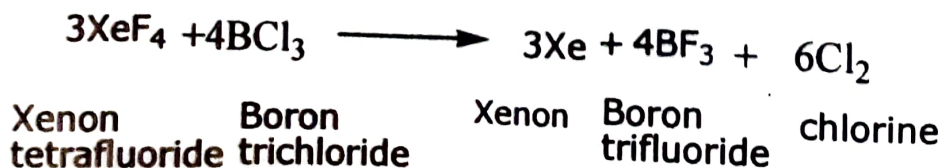
- 2) It is also synthesized by passing an electric discharge through a mixture of xenon & fluorine in 1:2 ratio at -80°C .

Properties :

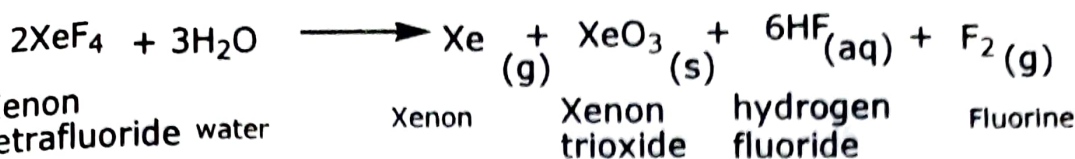
- 1) It is colourless crystalline solid which melts at 117°C it sublime easily
- 2) It is soluble in HF without reacting.
- 3) It is reduced by hydrogen at 117°C to give Xenon.



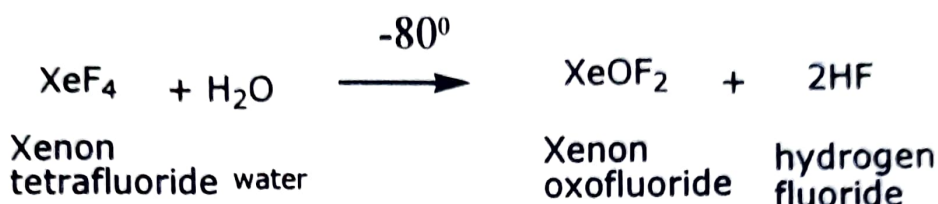
- 4) It reacts with boron trichloride to form boron trifluoride



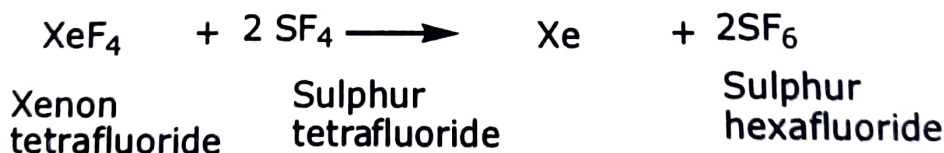
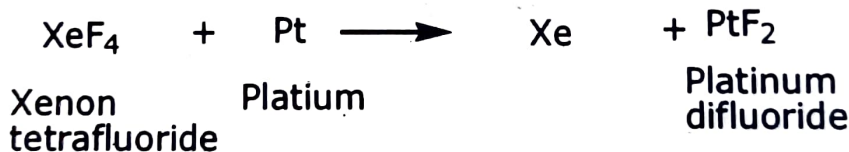
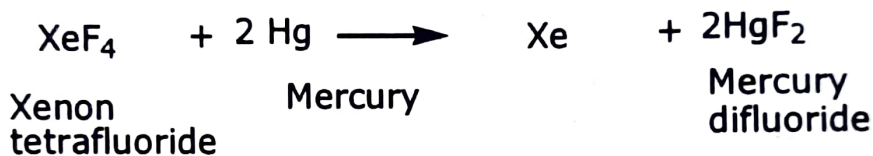
- 5) It undergoes disproportionation in water giving a highly explosive solid i.e. XeO_3 (xenon trioxide).



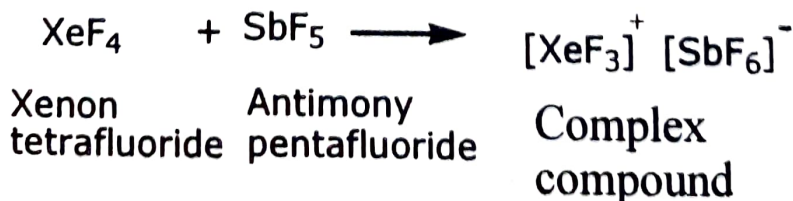
But when reaction is carried out at -80°C it forms xenon oxo fluoride.



- 6) It is a stronger fluorinating agent than XeF_2 . It converts Hg to HgF_2 , and NO_2F , SF_4 to SF_6



- 7) It forms addition compound with antimony pentafluoride.

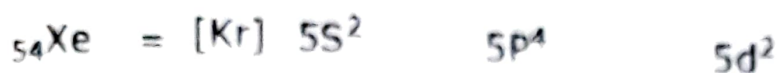
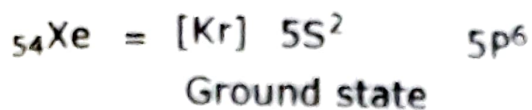


- 8) It combines with molten TaF_5 to form a straw coloured compound.



Structure of XeF_4 :-

- 1) In XeF_4 formation two of the 5 p electron go to the 5d orbital so there are four unpaired electron.
- 2) The six orbitals i.e. one 5s, three 5p and two 5d of Xe hybridise to form six, SP^3d^2 hybrid orbitals.
- 3) The covalent bond are formed by overlapping four of these hybrid orbital each contain one single electron. The two lone pairs occupy axial position to minimize electron pair repulsion and F-atom is placed at equatorial position and the molecule



Excited state



XeF_4 molecule

 sp^3d^2 hybridisation

Xenon hexafluoride(XeF_6):

Preparation :-

- 1) It is prepared by heating xenon with excess of fluorine in 1:20 ratio in a nickel vessel at $250-300^\circ\text{C}$ under 50-60 atm pressure
- 2) It can be obtained by interaction of XeF_4 and F_2 under pressure



xenon Fluorine Xenon hexafluoride

- 3) It is also prepared by passing electric discharge through a mix of Xenon and fluorine in 1:3 ratio at low temp.
- 4) It is extremely reactive so it cannot be stored in glass or quartz vessel because it give explosive XeO_3 .
- 5) On reaction with H_2 , NH_3 , or HCl it is reduced to xenon.

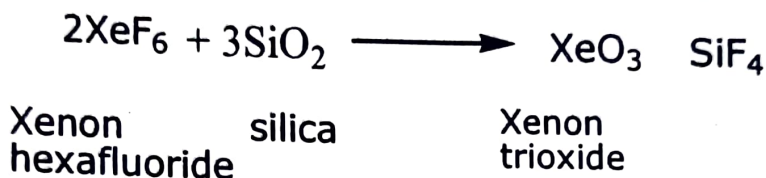
Properties :

- 1) It is crystalline solid substance which melts at 49.5°C

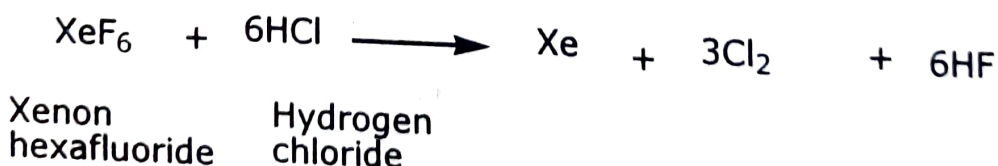
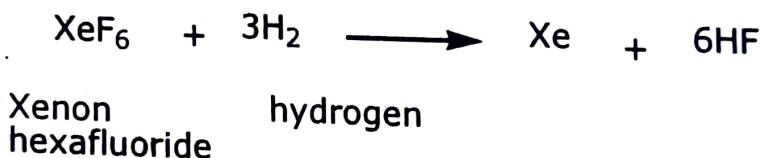
- 2) It is most volatile of all the fluoride of xenon Its vapour have a greenish yellow colour.
- 3) It dissolve hydrogen fluoride giving a solution which is good conductor of electricity.(it forms ions).



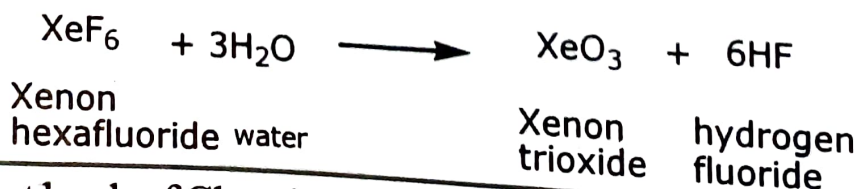
- 4) It is extremely reactive so it cannot be stored in glass or quartz vessel because it give explosive XeO_3 .



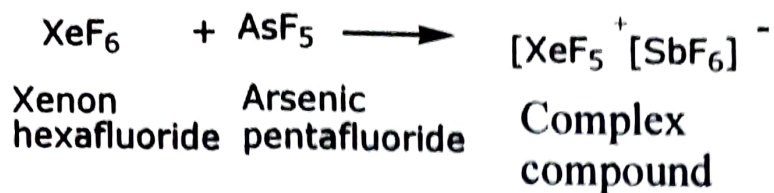
- 5) On reaction with H_2 , NH_3 , or HCl it is reduced to xenon.



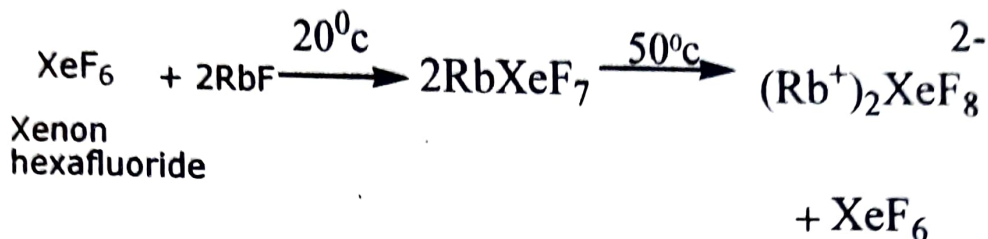
- 6) It undergoes slow hydrolysis with atmospheric moisture producing highly explosive XeO_3 .



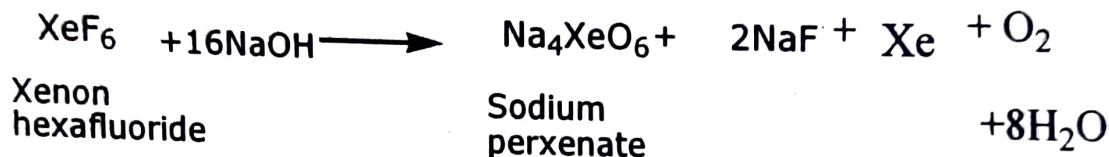
7) It reacts with fluoride ion acceptor to form adducts.



8) With alkali metal fluoride it form compounds containing XeF_7 , XeF_8^{2-} , ie it accepts F^- ion.

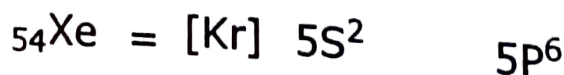


9) It reacts with alkali to give perxenates.

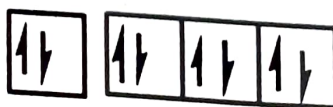


Structure of XeF_6 :

- 1) In the formation of XeF_6 three of the 5P electrons of Xe shifted to three 5d orbitals so that 6 unpaired electrons are present.
- 2) Seven orbitals ie. one S, three P and three d orbitals hybridise to give seven SP^3d^3 hybrid orbitals.
- 3) Six of these orbitals containing single e- are used in bonding with six atoms of fluorine.
- 4) It has been suggested that molecule has distorted octahedral structure.



Ground state





Excited state



Ground state



Excited state



XeF₆ molecule



 sp^3d^3 hybridisation

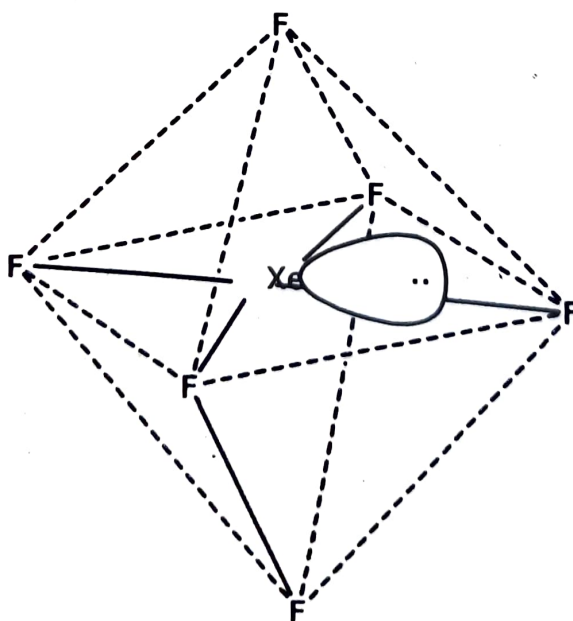


Fig. Distorted octahedral
 sp^3d^3 Hybridisation