

p-Block Elements

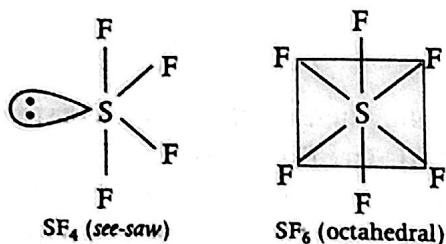
p-block elements are placed in group 13 to 18 of the periodic table. Their valence shell electronic configuration is ns^2np^{1-6} (except He which has $1s^2$ configuration). The first member of each of the groups (13-18 of the *p*-block elements) differ in many aspects from rest of the members of their respective groups. This anomalous behaviour is due to small size, high electronegativity and inability to expand its octet due to the absence of *d*-orbitals in the valence shell. We shall study about groups 16 to 18, one by one :

[TOPIC 1] Group 16 Elements (O, S, Se, Te, Po)

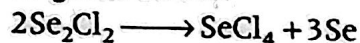
1.1 General Properties of Group 16 Elements and their Compounds

1. O, S, Se, Te and Po constitute group 16 of the periodic table. These are collectively known as chalcogens (ore forming). Their general valence shell electronic configuration is ns^2np^4 .
2. Atomic and ionic radii increases down the group while ionisation enthalpy and electronegativity decreases with increase in atomic number. Because of compact nature of oxygen atom, it has less negative electron gain enthalpy than sulphur. However, from sulphur onwards the value again becomes less negative upto polonium, Po.
3. The elements of group 16 have lower ionisation enthalpy values compared to those of group 15 in the corresponding periods, this is due to extra stable half-filled *p*-orbitals in group 15 elements.
4. The elements of group 16 show a number of oxidation states. Oxygen shows -2 oxidation state except in case of OF_2 ($+2$), O_2F_2 ($+1$) and H_2O_2 (-1). Other elements of this group exhibit $+2$, $+4$ and $+6$ oxidation states but $+4$ and $+6$ are common. The stability of $+6$ oxidation state decreases and $+4$ oxidation state increases down the group due to inert pair effect.
5. All these elements form H_2M (where, $M = O, S, Se, Te, Po$) type hydrides. Acidic character and reducing character of hydrides increases from H_2S to H_2Te . Bond dissociation enthalpy, thermal stability and HMH angle decreases down the group. Boiling points increase from H_2S to H_2Te . H_2O has extraordinarily high boiling point due to intermolecular H-bonding. H_2O does not possess reducing property.
6. These elements form MO_2 and MO_3 (where, $M = S, Se, Te, Po$) type oxides. SO_2 is reducing while TeO_2 is an oxidising agent. Both types of oxides are acidic in nature.

7. These elements form MX_2 , MX_4 and MX_6 type halides ($X = F, Cl, Br$ and I). All hexafluorides are gaseous and octahedral in shape. SF_6 is exceptionally stable for steric reasons. MX_4 (SF_4, SeF_4 , etc.) type halides have sp^3d -hybridisation and have **trigonal bipyramidal structure** in which one of the equatorial positions is occupied by a lone pair of electrons (*see-saw geometry*).

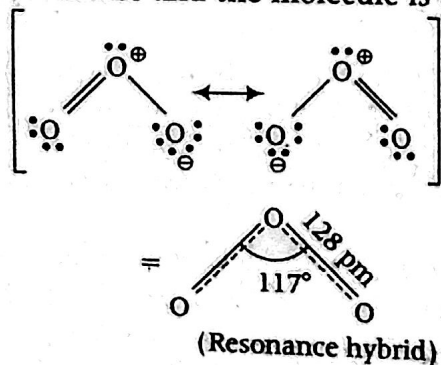


8. **Dihalides** are sp^3 -hybridised and have tetrahedral shape. Examples are S_2F_2 , S_2Cl_2 , S_2Br_2 , Se_2Cl_2 and Se_2Br_2 . These dimeric halides undergo disproportionation as given below:



9. Oxygen is the first member of Group 16 with electronic configuration $1s^2, 2s^2 2p^4$. O_2 and O_3 are its most important compounds.

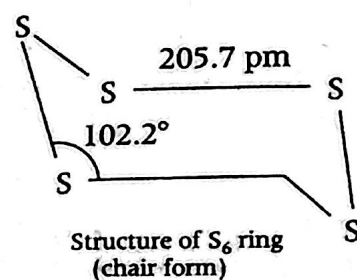
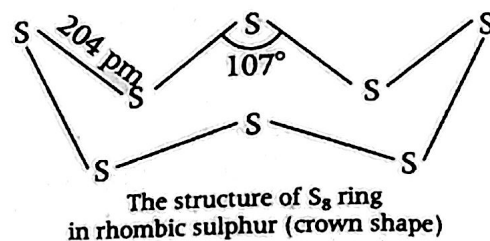
- (i) Dioxygen (O_2) in vapour state is **paramagnetic** in nature.
- (ii) Ozone is an allotropic form of oxygen. Due to the ease with which it liberate atoms of nascent oxygen, it acts as a powerful oxidising agent.
- (iii) The two oxygen-oxygen bond lengths in O_3 molecule is identical due to resonance and the molecule is angular.



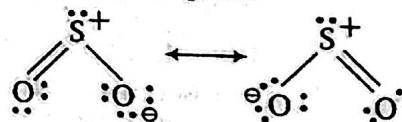
10. The second member of group 16 is sulphur. Sulphur (S_2) in vapour state is also **paramagnetic** in nature. Its main oxides

are SO_2 and SO_3 . Sulphur also form many important oxo-acids. (e.g. H_2SO_4).

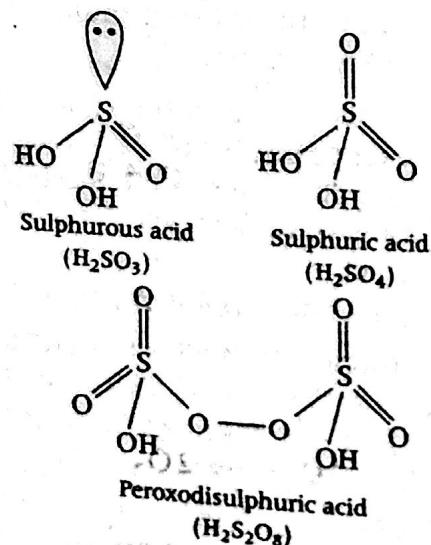
- (i) Both allotropes of S, i.e. rhombic and monoclinic sulphur have S_8 molecules. The S_8 ring in both the forms is puckered and has a crown shape. In cyclo S_6 , the ring adopts the chair form.

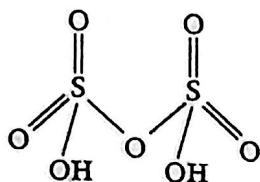


- (ii) SO_2 is produced as a by-product of the roasting of sulphide ores. It behaves as a reducing agent (when moist). The two S—O bonds in SO_2 molecule are equal due to two resonating structures. SO_2 molecule is angular.



- (iii) Structures of some important oxoacids of sulphur are given below:

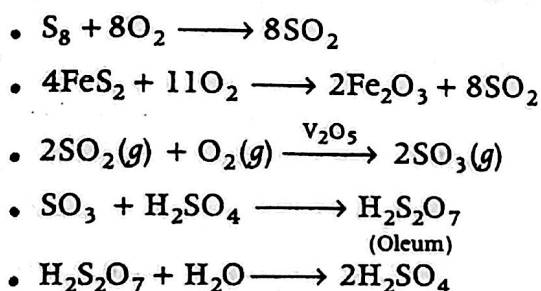




Pyrosulphuric acid (Oleum)
($\text{H}_2\text{S}_2\text{O}_7$)

- (iv) Sulphuric acid is manufactured by **contact process**. It forms two series of salts; normal sulphates and acid sulphates. The larger value of K_a indicates that H_2SO_4 is largely dissociated into H^+ and HSO_4^- ions. Greater the value of K_a , the stronger is the acid.

Contact process involves following steps:

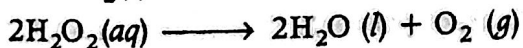
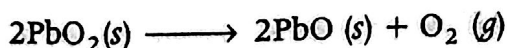
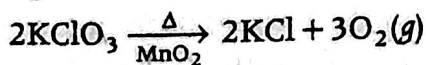


- (v) Concentrated H_2SO_4 acts as a strong dehydrating agent. It removes water even from organic compounds.

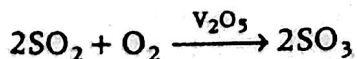
1.2 Important Reactions of Group 16 Compounds

- (i) For dioxygen (O_2)

Preparations



Oxidising property

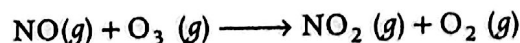
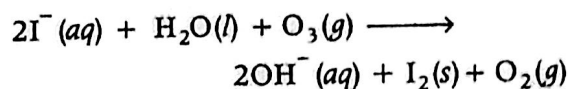
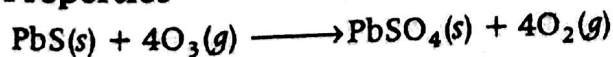


- (ii) For ozone (O_3)

Preparation

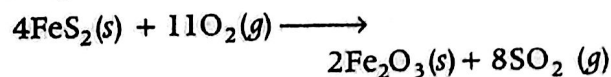


Properties

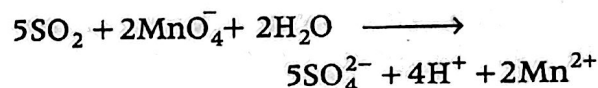
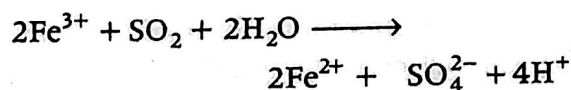
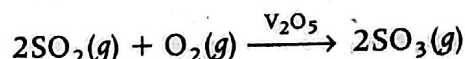
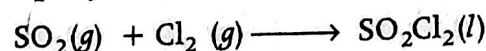
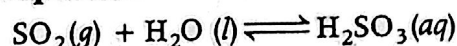


- (iii) For sulphur dioxide (SO_2)

Preparation

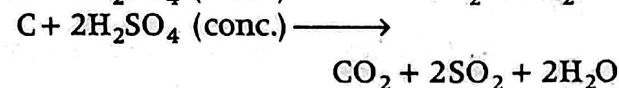
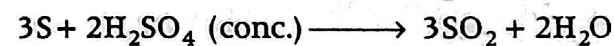
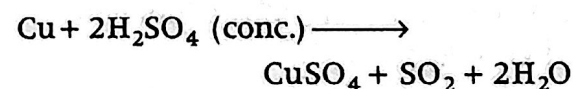
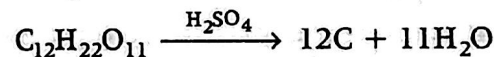


Properties



- (iv) For sulphuric acid (H_2SO_4)

Properties



[TOPIC 2] Group 17 Elements (F, Cl, Br, I and At)

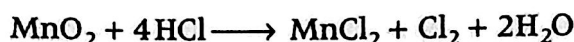
2.1 General Properties of Group 17 Elements and their Compounds

1. F, Cl, Br, I and At are the elements of group 17. These are collectively known as halogens. At (astatine) is a radioactive element. Their general valence shell configuration is ns^2np^5 .
2. Halogens have smallest atomic radii in their respective periods due to maximum effective nuclear charge. Atomic and ionic radii increases from fluorine to iodine.
3. Halogens have high ionisation enthalpy because they have very little tendency to lose electron.
4. Halogens have maximum negative electron gain enthalpy in the corresponding periods because they have only one electron less than stable noble gas configuration. On moving down the group, it becomes less negative. However, negative electron gain enthalpy of fluorine is less than that of chlorine. It is due to small size of fluorine atom and high electron density. As a result of this, there are strong interelectronic repulsions and the incoming electron (in $2p$ -orbital) does not experience much attraction.
5. Halogens are coloured due to absorption of radiations in visible region which results in excitation of valence shell electrons to higher energy level.
6. The decreasing order of bond dissociation enthalpies is $\text{Cl—Cl} > \text{Br—Br} > \text{F—F} > \text{I—I}$. Smaller dissociation enthalpy of F_2 in comparison to Cl_2 shows that there is relatively large electron-electron repulsion between the lone pairs in F_2 molecule due to its small size.
7. All halogens exhibit -1 oxidation state. However, Cl, Br, I exhibits $+1$, $+3$, $+5$ and $+7$ oxidation states also. F exhibits only -1 oxidation state because it has no vacant d -orbitals in its valence shell.
8. Halogens are strong oxidising agent, it is due to easy acceptance of an electron. F_2 is the strongest oxidising halogen and it oxidises other halide ions in solution or even in solid phase.
$$\text{F}_2 + 2\text{X}^- \longrightarrow 2\text{F}^- + \text{X}_2 \quad (\text{X} = \text{Cl, Br or I})$$
$$\text{Cl}_2 + 2\text{X}^- \longrightarrow 2\text{Cl}^- + \text{X}_2 \quad (\text{X} = \text{Br or I})$$
$$\text{Br}_2 + 2\text{I}^- \longrightarrow 2\text{Br}^- + \text{I}_2$$
9. Halogens form HX type hydrogen halides with hydrogen. Thermal stability and bond dissociation enthalpy decreases down the group from HF to HI but acidic strength increases from HF to HI. Their boiling points also increase from HCl to HI. High boiling point of HF is due to the intermolecular H-bonding.

10. OF_2 and O_2F_2 both are strong fluorinating agents and are called oxygen fluorides. O_2F_2 is used in removing Pu as PuF_6 from spent nuclear fuel. Cl, Br and I form oxides in which halogens exist as +1 to +7 states.

11. Chlorine is one of the most important member of this family. Chlorine is a greenish yellow gas with pungent and suffocating odour. It is manufactured by Deacon's process or by the electrolysis of brine (liberated at anode). It is a powerful bleaching agent and bleaching action is due to oxidation (in the presence of moisture). It is used in sterilising drinking water and in the preparation of poisonous gases such as phosgene (COCl_2), tear gas (CCl_3NO_2), mustard gas ($\text{ClCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{Cl}$), etc.

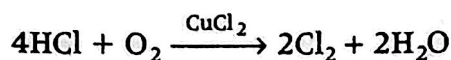
Preparation



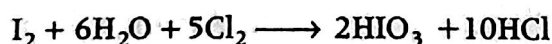
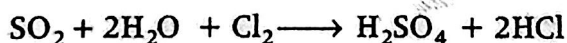
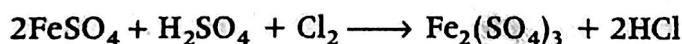
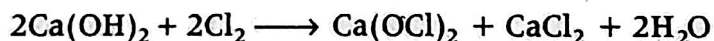
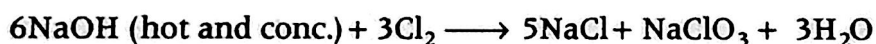
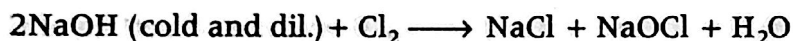
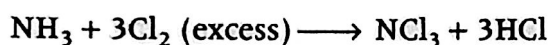
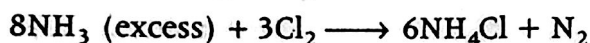
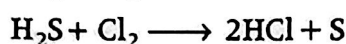
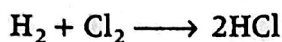
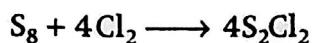
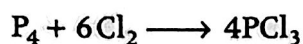
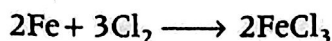
Deacon's process



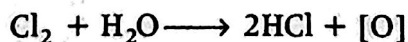
Deacon's process



Properties



Bleaching action

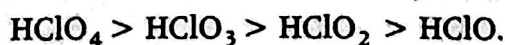


Coloured substance + $[\text{O}] \longrightarrow$ Colourless substance

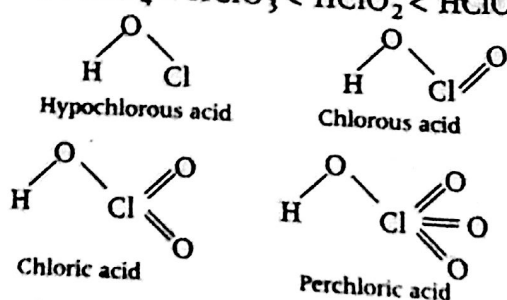
12. Aqueous solution of hydrogen chloride is hydrochloric acid. A mixture of conc. HCl and conc. HNO_3 (3:1 ratio) is known as *aqua-regia* which is used to dissolve noble metals such as Au, Pt, etc. When conc. HCl reacts with finely powdered iron, ferrous chloride is formed. Liberation of H_2 prevents the formation of ferric chloride. Oxo-acids of halogen are important class of compound.

13. Fluorine forms only one oxoacid, i.e. HOF due to high electronegativity and small size of F. The other halogens form several oxoacids such as HOX, HOXO, HOXO₂, HOXO₃.

(i) Order of acidic strength of oxoacids of the same halogen is

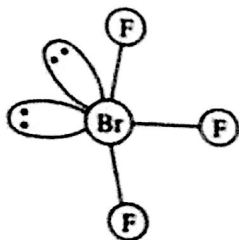


(ii) Oxidising power of oxoacids of chlorine is $\text{HClO}_4 < \text{HClO}_3 < \text{HClO}_2 < \text{HClO}$.

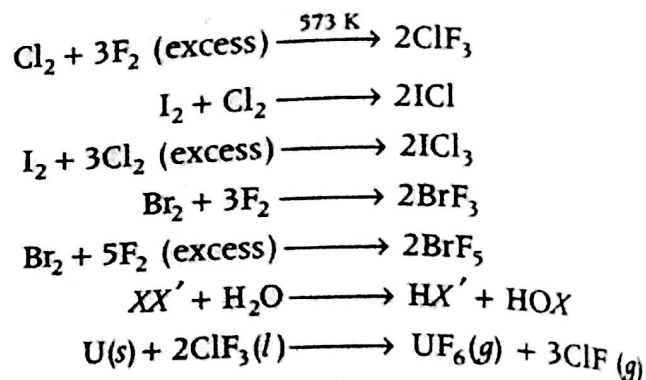


Structures of oxoacids of chlorine

14. Halogens combine amongst themselves to form a number of compounds known as interhalogen compounds of the types XX' , XX'_3 , XX'_5 , and XX'_7 (here, X is larger size halogen and X' is smaller size halogen). These are more reactive than halogens except fluorine. On the basis of VSEPR theory, XX'_3 compounds have the bent T-shape, XX'_5 compounds have square pyramidal and XX'_7 has pentagonal bipyramidal structure.

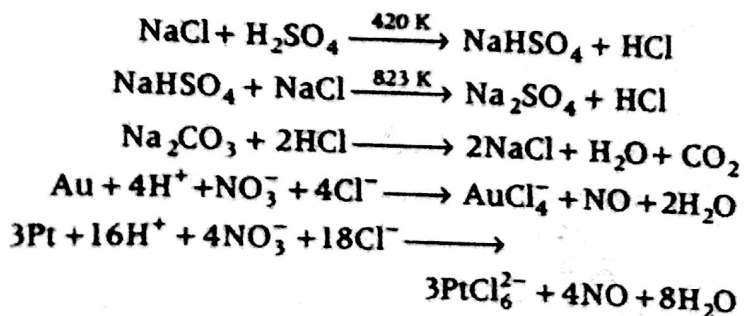


Interhalogen compounds can be used as non-aqueous solvents, fluorinating agents etc. ClF_3 and BrF_3 are used for the production of UF_6 in the enrichment of ^{235}U .

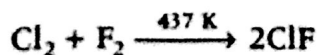


2.2 Important Reactions of Halogen Compounds

For hydrochloric acid (HCl)



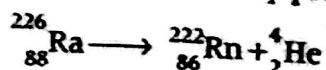
Interhalogen compounds



[TOPIC 3] Group 18 Elements (He, Ne, Ar, Kr, Xe and Rn)

3.1 General Properties of Group 18 Elements and their Compounds

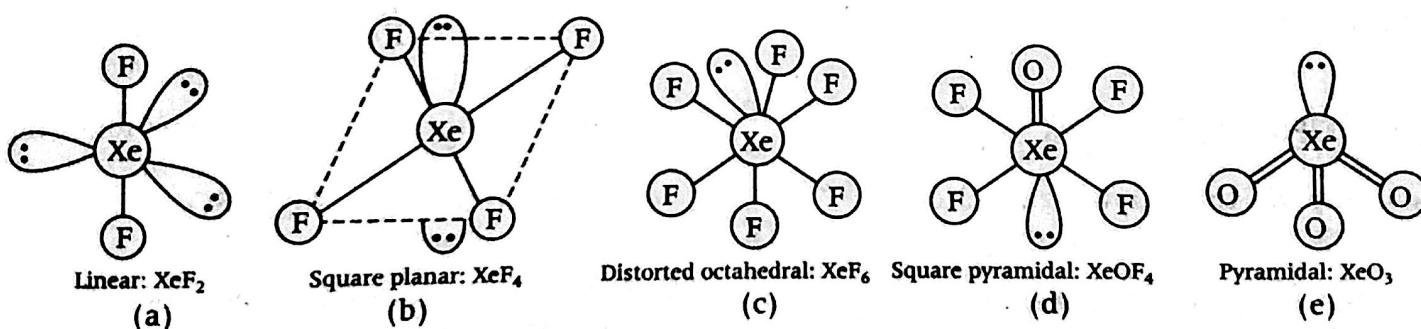
1. He, Ne, Ar, Kr, Xe and Rn are the elements of group 18. These are chemically unreactive so, these are termed as noble gases. All the noble gases except radon (Rn) occur in the atmosphere (~ 1% by volume) while radon is obtained as a decay product of radium (^{226}Ra).



2. General valence shell electronic configuration of all noble gases is ns^2np^6 except He which has $1s^2$ configuration.
3. Due to stable electronic configuration, these gases exhibit very high ionisation enthalpy which decreases down the group with the increase in atomic size.

- Atomic radii increases down the group with increase in atomic number.
- These gases have large positive values of electron gain enthalpy because these have no tendency to accept the electron.
- Melting and boiling points of noble gases are very low because there are only one type of interatomic interaction, i.e. weak dispersion forces.
- The inertness of noble gases to chemical reactivity is due to
 - stable ns^2np^6 configuration (except He that has stable $1s^2$ configuration).
 - high ionisation enthalpy and more positive electron gain enthalpy.
- Xenon was the first element which form compounds with oxygen and fluorine. In 1962, Neil Bartlett first prepared a red compound which is formulated as $O_2^+ PtF_6^-$. He then realised that the first ionisation enthalpy of molecular oxygen was almost identical with that of Xenon. This observation made Neil Bartlett to prepare another red colour compound $Xe^+ PtF_6^-$ by mixing PtF_6 and Xe.
- Xenon has least ionisation enthalpy (except radon which is radioactive) among noble gases, therefore it forms compounds with oxygen and fluorine readily which are the most electronegative elements.
- Xenon forms three binary fluorides, XeF_2 , XeF_4 , and XeF_6 . Hydrolysis of XeF_4 and XeF_6 gives XeO_3 . Partial hydrolysis of XeF_6 gives $XeOF_4$ and XeO_2F_2 .
- XeF_2 -linear, XeF_4 -square planar, XeF_6 -distorted octahedral, $XeOF_4$ -square pyramidal and XeO_3 -pyramidal in shape.

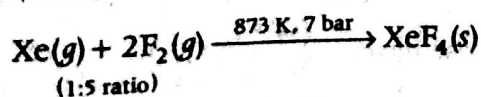
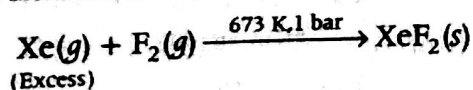
Structures of some xenon compounds

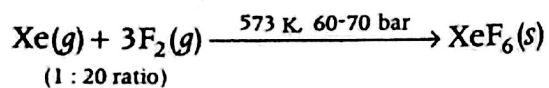


- Uses of inert gases** Ar is used to provide an inert atmosphere (e.g. incandescent bulb), helium is used in filling meteorological balloons and as a diluent for oxygen in modern diving apparatus, neon is used in discharge tubes and fluorescent bulbs for display in advertisement.

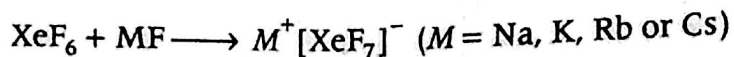
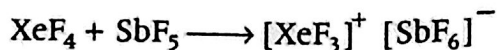
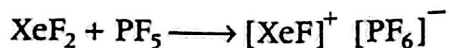
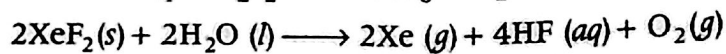
3.2 Important Reactions of Xenon and Its Compounds

(i) Preparation of xenon-fluorine compound





Properties



(ii) Preparation of xenon-oxygen compound

