7: The p-Block Elements

A. Introduction: Elements in which the last electron enters in the any one of the three p- orbital of their outermost shells. Gen. electronic configuration of outer shell is ns^2np^{1-6}

GROUP 15: The Nitrogen Family

B. Atomic and Physical Properties:

1. Outer Electronic Configuration: ns^2np^3

2. Group members: Nitrogen (N), Phosphorus (P), As (Arsenic), Sb(Antimony), Bi (Bismuth).

3. Atomic and ionic radii: Atomic radii increase on going down the group due to addition of a new shell. There is appreciable increase in atomic radii from N to P. There is small increase from As to Bi due to presence of completely filled d or f orbitals in heavy elements.

4. Ionization energies: On moving down the group, IE decreases due to increase in atomic size. Group 15 elements have higher ionisation energy than group 14 elements due to smaller size of group 15 elements. Group 15 elements also have higher ionization energy than group 16 elements because they have stable electronic configuration i.e., half filled p-orbitals.

$$B < C < O < N < F < Ne$$

5. Electronegativity: These are more electronegative than the corresponding elements of group 14 due to greater effective nuclear charge. On moving down the group, IE decreases due to increase in atomic size.

6. Allotropy: All elements of Group 15 except nitrogen show allotropy.

7. Metallic character: Increases down the group due to decreases IE and increases in atomic size. Thus N and P are non metals. As and Sb are metalloids while Bi is typical metal.

8. Catenation: Nitrogen shows catenation to some extent due to triple bond but phosphorus shows catenation to maximum extent. The tendency to show catenation decreases down the group.

9. Density: The density increases regularly down the group as usual.

10. Oxidation states:

- The common oxidation states are +3, +5 and -3. Only N exhibits all the oxidation states from -3 to +5.
- As we move down the group, the tendency to exhibit -3 oxidation state decreases due to decrease in electronegativity.
- As we move down the group, the tendency to exhibit +5 oxidation state also decreases where as the tendency to attain +3 oxidation state increases due to inert pair effect.
- Nitrogen and phosphorus with oxidation states from +1 to +4 undergo oxidation as well as reduction in acidic medium. This process is called disproportionation.

$$3\,HNO_2 \rightarrow HNO_3 + H_2O + 2\,NO$$

- Inert Pair Effect: It is the tendency of the electrons in the outermost atomic s orbital to remain unionized or unshared in compounds of post- transition metals.

C. Chemical Properties of Group 15 Elements:

1. Reactivity towards hydrogen (Hydrides): All group 15 members form trihydrides, EH_3. It belongs to sp^3 hybridisation.

a) **Thermal stability:** Thermal stability of hydrides decreases down the group due to decreases in bond dissociation energy down the group.

$$NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$$

b) **Boiling point:** It increases with increase in size due to increase in van der Waals forces. Boiling point of NH_3 is more because of hydrogen bonding.

$$PH_3 < AsH_3 < NH_3 < SbH_3 < BiH_3$$

c) **Bond angle:** Electronegativity of N is highest. Therefore, the lone pairs will be towards nitrogen and hence more repulsion between bond pairs. Therefore bond angle is the highest. After nitrogen, the electronegativity decreases down the group so decreasing order of bond angle is:

$$NH_3\ (107.8°) > PH_3\ (99.5°) > AsH_3\ (91.8°) \approx SbH_3\ (91.3°) > BiH_3\ (90°)$$

d) **Basicity:** It decreases down the group because the lone pair of electrons are more concentrated on nitrogen and hence the basicity will be maximum in the case of NH_3. The basic character order is:

$$NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$$

e) **Reducing power:** The reducing power of hydrides increases down the group due to decrease in bond dissociation energy down the group.

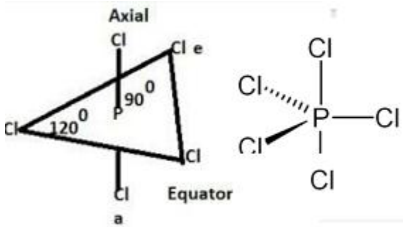
2. Reactivity towards oxygen (Oxide): All group 15 elements form trioxides (M_2O_3) and pentoxides (M_2O_5). Acidic character of oxides decreases and basicity increases down the group. This is because the size of nitrogen is very small. It has a strong positive field in a very small area. Therefore, it attracts the electrons of water's O-H bond to itself and release H^+ ions easily.

3. Reactivity towards halogen (Halide): Group 15 elements form tri halides and penta halides.

a) Tri halides: These are covalent compounds and become ionic down the group. It's having sp^3 hybridisation and pyramidal shape.

b) Penta halides:

- In PC$_{15}$, there are three equatorial bonds and two axial bonds. The axial bonds are longer than equatorial bonds because of greater repulsion from equatorial bonds.



- They are lewis acids because of the presence of vacant d – orbitals. They posses sp^3d hybridisation and trigonal bipyramidal shape.

$$PCl_5 + Cl^- \rightarrow [PCl_6]^-$$

- PCl_5 is ionic in solid state and exist as $[PCl_4]^+ [PCl_6]^-$ in which the cation is tetrahedral and the anion is octahedral.
- Nitrogen does not form pentahalides due to absence of *d*- orbitals.

4. Reactivity towards metals: All elements react with metals to form binary compounds (M_3E_2 type) in –3 oxidation state for example Ca_3N_2 (calcium nitride), Ca_3P_2 (calcium phosphide) etc.

5. Anomalous behaviour of Nitrogen: The behaviour of nitrogen differs from rest of the elements due to the following reason:

- It has a small size.
- It does not have d – orbitals
- It has high electronegativity
- It has high ionization enthalpy

5. Dinitrogen (N_2):

a) Preparation: Commercially dinitrogen is produced by the liquefaction and fractional distillation of air. Some other laboratory methods are as following-

$$NH_4Cl(aq) + NaNO_2(aq) \xrightarrow{heat} N_2(g) + 2H_2O(l) + NaCl(aq)$$

$$(NH_4)_2Cr_2O_7 \xrightarrow{heat} N_2 + 4H_2O + Cr_2O_3$$

$$Ba(N_3)_2 \xrightarrow{heat} Ba + 3N_2$$

b) Properties:

- It is a colorless, odourless, tasteless and non – toxic gas. It is chemically un-reactive at ordinary temperature due to triple bond in $N \equiv N$ which has high bond dissociation energy.
- It form nitrides with highly electropositive metals like Li, Ca and Mg

$$3Mg + N_2 \rightarrow Mg_3N_2$$

$$6Li + N_2 \rightarrow 2Li_3N$$

- It combine with O_2 at about 2000K and to form nitric oxide, NO.

$$N_2 + O_2(g) \rightarrow 2NO(g)$$

6. Ammonia (NH_3): Ammonia molecule is trigonal pyramidal with nitrogen atom at the apex. It has 3 bond pairs and 1 lone pair. N is sp^3 hybridised.

a) Preparation (By Haber's Process): Reaction conditions are Pressure 200 x 10^5 Pa, temperature 773 K and catalyst is FeO with small amount of K_2O and Al_2O_3.

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g) \qquad \Delta_f H^0 = -46.1 kJ\ mol^{-1}$$

b) Properties: It is extremely soluble in water. It acts as lewis base due to presence of lone pair of electrons on nitrogen and hence forms a number of complexes with metal ions.

$$Cu^{2+} + 4NH_3 \rightarrow [Cu(NH_3)_2]^{2+}$$

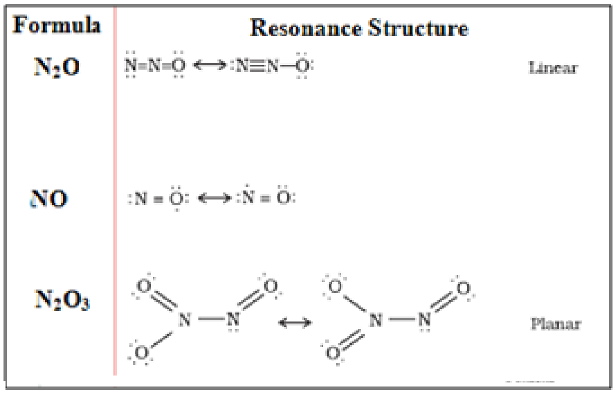
$$AgCl\ (s) + 2NH_3\ (aq) \rightarrow [Ag(NH_3)_2]Cl\ (aq)$$

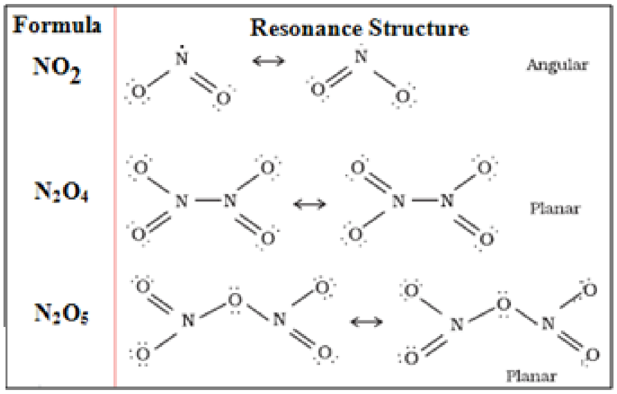
White ppt colourless

7. Oxides of Nitrogen: The oxide in higher oxidation state is more acidic than that of lower oxidation state

Name	Formula	Oxidation state of nitrogen	Common methods of preparation	Physical appearance and chemical nature
Dinitrogen oxide [Nitrogen(I) oxide]	N_2O	+ 1	$NH_4NO_3 \xrightarrow{Heat} N_2O + 2H_2O$	colourless gas, neutral
Nitrogen monoxide [Nitrogen(II) oxide]	NO	+ 2	$2NaNO_2 + 2FeSO_4 + 3H_2SO_4 \rightarrow Fe_2(SO_4)_3 + 2NaHSO_4 + 2H_2O + 2NO$	colourless gas, neutral
Dinitrogen trioxide [Nitrogen(III) oxide]	N_2O_3	+ 3	$2NO + N_2O_4 \xrightarrow{250\,K} 2N_2O_3$	blue solid, acidic
Nitrogen dioxide [Nitrogen(IV) oxide]	NO_2	+ 4	$2Pb(NO_3)_2 \xrightarrow{673\,K} 4NO_2 + 2PbO$	brown gas, acidic
Dinitrogen tetroxide [Nitrogen(IV) oxide]	N_2O_4	+ 4	$2NO_2 \underset{Heat}{\overset{Cool}{\rightleftharpoons}} N_2O_4$	colourless solid/ liquid, acidic
Dinitrogen pentoxide [Nitrogen(V) oxide]	N_2O_5	+5	$4HNO_3 + P_4O_{10} \rightarrow 4HPO_3 + 2N_2O_5$	colourless solid, acidic

Resonance Structure of Oxide of Nitrogen:





8. Oxo-acids of Nitrogen: Oxo-acids of nitrogen are Hypo nitrous acid ($H_2N_2O_2$), nitrous acid (HNO_2) and nitric acid (HNO_3).

Nitric Acid (HNO_3):

a) Preparation (By Ostwald Process):

$$4NH_3 + 5O_2 \xrightarrow{Pt/Rh \text{ gauge } 500k,\ 9 \text{ bar}} 4NO + 6H_2O$$

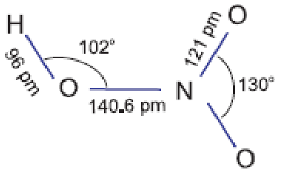
$$2NO + O_2 \rightarrow 2NO_2$$

$$3NO_2(g) + H_2O(l) \rightarrow 2HNO_3(aq) + NO(g)$$

NO thus formed is recycled and the aqueous HNO_3 can be concentrated by distillation upto ~ 68% by mass. Further concentration to 98% can be achieved by dehydration with concentrated H_2SO_4.

b) Properties:

- It is colorless (pure) while the impure acid is yellow due to presence of NO_2 as impurity. Nitric acid containing dissolved nitrogen dioxide is known as fuming nitric acid.
- In the gaseous state, nitric acid exists as a planar molecule.



- In an aqueous solution, it behaves as a strong acid giving hydronium and nitrate ions.

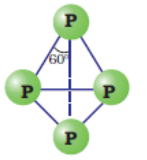
$$HNO_3(aq) + H_2O(l) \rightarrow H_3O^+(aq) + NO_3^-(aq)$$

- Nitric acid is strong oxidizing agent and attack most metals except noble metals like gold and platinum.
- Metal such as Al, Cr not dissolves in concentrated nitric acid b/c of the formation of a passive film of oxide on the surface.

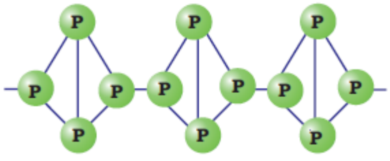
9. Phosphorus: It shows the property of catenation to maximum extent due to most stable P – P bond. It has many allotropes, the important ones are:

(i) White phosphorus (ii) Red phosphorus (iii) Black phosphorus

Structure of white and red phosphorus:

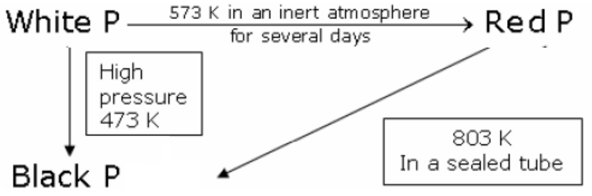


White phosphorus



Red phosphorus

Preparation:



Sr. No.	Property	White Phosphorus	Red Phosphorus	Black Phosphorus
1	State	Translucent white waxy solid	Iron grey luster powder	Opaque monoclinic or rhombohedral crystals
2	Structure	Discrete tetrahedral P_4 molecules	Polymeric structure consisting of chains of P_4 units linked together	Exists in two forms - α black P and β black P
3	Reactivity	Very reactive	less reactive than white phosphorus	Very less reactive
4	Physiological action	Poisonous	Non-poisonus	~
5	Solubility	Insoluble in water but soluble in CS_2	Insoluble in water as well as CS_2	~
6	Action of air	Greenish Glow in dark due to readily catches fire in air.	Does not glow in dark	~
7	Action of alkali	PH3 is formed	No reaction	~
8	Action of chlorine	PCl_3 or PCl_5 is formed	On heating PCl_3 or PCl_5 formed	~
9		It has low ignition temperature, therefore, kept under water	~	~

10. Phosphine:

Preparation:

$$\underset{\text{Calcium Phosphide}}{Ca_3P_2} + 6H_2O \rightarrow \underset{\text{Calcium Hydroxide}}{3Ca(OH)_2} + \underset{\text{Phosphine}}{2PH_3}$$

$$Ca_3P_2 + 6HCl \rightarrow 3CaCl_2 + 2PH_3$$

$$P_4 + 3NaOH + 3H_2O \rightarrow \underset{\text{Sodium Hypophosphite}}{3NaH_2PO_2} + \underset{\text{Phosphine}}{PH_3}$$

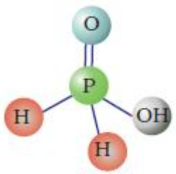
Properties:

- It is highly poisonous, colourless gas and has a smell of rotten fish. It is slightly soluble in water.
- PH_3 reacts with acids like HBr to form PH_4Br (phosphonium compound) which show that it is basic in nature.

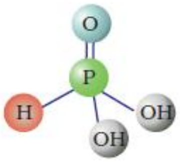
$$PH_3 + HBr \rightarrow PH_4Br$$

- The spontaneous combustion of phosphine is technically used in Holme's signal. It is also used in smoke screens.

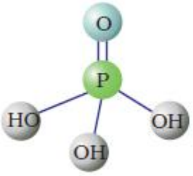
11. Oxoacids of Phosphorus:



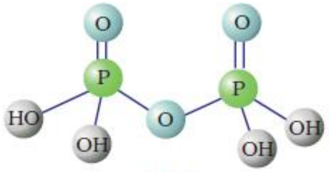
H_3PO_2
Hypophosphorous acid



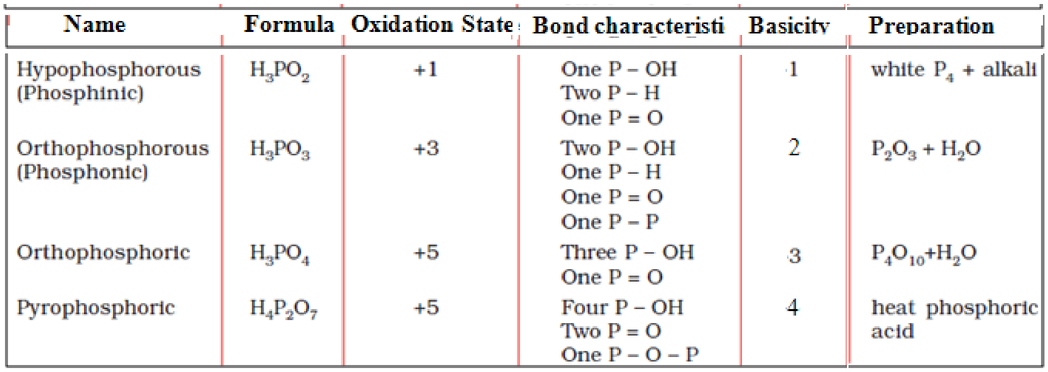
H_3PO_3
Orthophosphorous acid



H_3PO_4
Orthophosphoric acid



$H_4P_2O_7$
Pyrophosphoric acid



Name	Formula	Oxidation State	Bond characteristi	Basicity	Preparation
Hypophosphorous (Phosphinic)	H_3PO_2	+1	One P – OH Two P – H One P = O	1	white P_4 + alkali
Orthophosphorous (Phosphonic)	H_3PO_3	+3	Two P – OH One P – H One P = O One P – P	2	$P_2O_3 + H_2O$
Orthophosphoric	H_3PO_4	+5	Three P – OH One P = O	3	P_4O_{10}+H_2O
Pyrophosphoric	$H_4P_2O_7$	+5	Four P – OH Two P = O One P – O – P	4	heat phosphoric acid

Properties:

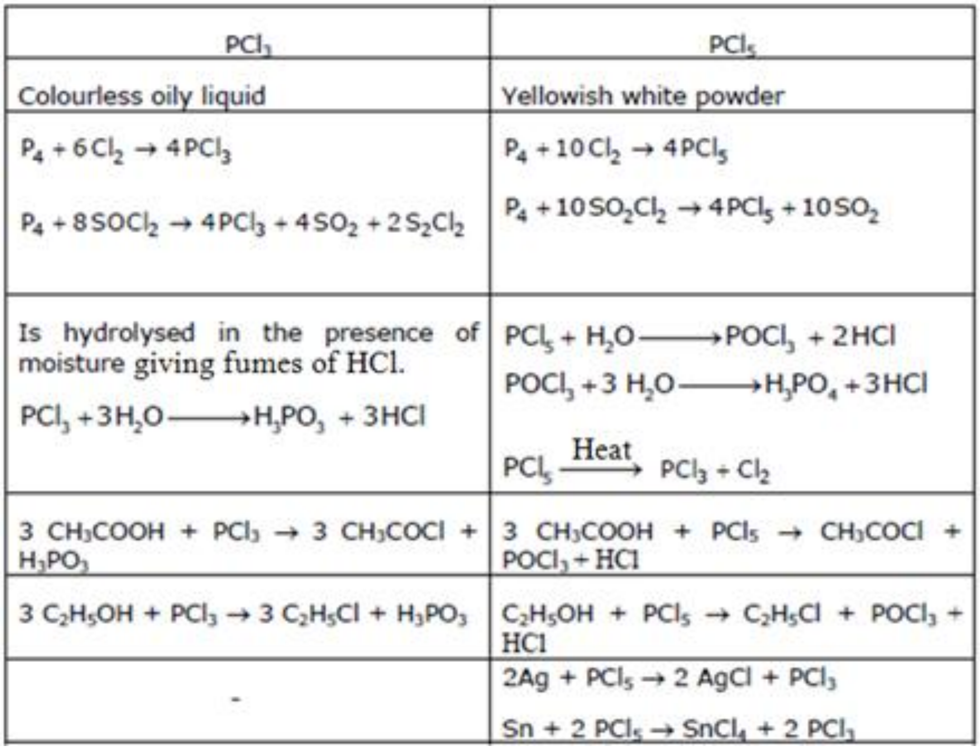
- On heating, orthophosphorus acids disproportionate to give orthophosphoric acid and phosphine.

$$4H_3PO_3 \rightarrow 3H_3PO_4 + PH_3$$

- The acids which contain P-H bond have strong reducing properties. So hypophosphorous acid is a good reducing agent as it contains two P-H bonds so it easily reduces AgNO3 to metallic Ag.

$$4\ AgNO_3 + 2H_2O + H_3PO_2 \rightarrow 4Ag + 4HNO_3 + H_3PO_4$$

12. Phosphorus Halides:



PCl_3	PCl_5
Colourless oily liquid	Yellowish white powder
$P_4 + 6Cl_2 \rightarrow 4PCl_3$ $P_4 + 8SOCl_2 \rightarrow 4PCl_3 + 4SO_2 + 2S_2Cl_2$	$P_4 + 10Cl_2 \rightarrow 4PCl_5$ $P_4 + 10SO_2Cl_2 \rightarrow 4PCl_5 + 10SO_2$
Is hydrolysed in the presence of moisture giving fumes of HCl. $PCl_3 + 3H_2O \longrightarrow H_3PO_3 + 3HCl$	$PCl_5 + H_2O \longrightarrow POCl_3 + 2HCl$ $POCl_3 + 3\ H_2O \longrightarrow H_3PO_4 + 3HCl$ $PCl_5 \xrightarrow{Heat} PCl_3 + Cl_2$
$3\ CH_3COOH + PCl_3 \rightarrow 3\ CH_3COCl + H_3PO_3$	$3\ CH_3COOH + PCl_5 \rightarrow CH_3COCl + POCl_3 + HCl$
$3\ C_2H_5OH + PCl_3 \rightarrow 3\ C_2H_5Cl + H_3PO_3$	$C_2H_5OH + PCl_5 \rightarrow C_2H_5Cl + POCl_3 + HCl$
-	$2Ag + PCl_5 \rightarrow 2\ AgCl + PCl_3$ $Sn + 2\ PCl_5 \rightarrow SnCl_4 + 2\ PCl_3$

GROUP 16: The Oxygen Family

A. Atomic and Physical Properties:

1. Outer Electronic Configuration: ns^2np^4

2. Group members: Oxygen (O), sulphur (S), selenium (Se), tellurium (Te) and polonium (Po).

3. Oxidation states:

- They show -2, +2, +4, +6 oxidation states.
- Oxygen does not show +6 oxidation states due to absence of d – orbitals.
- Po does not show +6 oxidation states due to inert pair effect.
- The stability of -2 oxidation state decreases down the group due to decrease in electronegativity.
- Oxygen shows -2 oxidation state in general except in OF_2 and O_2F_2
- The stability of +6 oxidation state decreases and +4 oxidation state increases due to inert pair effect.

4. Ionisation enthalpy: Decreases down the group while ionisation enthalpy of group 16 elements is lower than group 15 due to half filled p-orbitals in group 15 which is more stable.

5. Electron gain enthalpy: Oxygen has less negative electron gain enthalpy than S because of small size of O. From S to Po electron gain enthalpy becomes less negative to Po because of increase in atomic size like S > O > Se > Te > Po

6. Melting and boiling point: It increases down the group due to increase in size and hence greater Vander walls forces. Oxygen has much lower melting and boiling points than sulphur because oxygen is diatomic (O_2) and sulphur is octatomic (S_8).

The last element Po, has lower melting and boiling point than Te b/c of maximum inert pair effect.

B. Chemical Properties of Group 16 Elements:

1. Reactivity with hydrogen (Hydride): All group 16 elements form hydrides of the formula H_2E. They posses bent shape and sp^3 hybridisation.

a) Acidic nature: It increases down the group b/c they can dissociate more easily to give H^+ ions.

$$H_2O < H_2S < H_2Se < H_2Te$$

b) Thermal stability: It decreases down the group b/c as the size of atom increases the bond dissociation enthalpy decreases.

$$H_2O > H_2S > H_2Se > H_2Te > H_2Po$$

c) Reducing character: Except H2O, all are reducing agents. It increases down the group b/c as the size of atom increases the bond dissociation enthalpy decreases.

$$H_2O < H_2S < H_2Se < H_2Te < H_2Po$$

d) H_2O is a liquid while H_2S is a gas. This is because strong hydrogen bonding is present in water. This is due to small size and high electronegativity of O.

2. Reactivity with oxygen (Oxides): EO_2 and EO_3

a) Reducing character: Reducing character of dioxides decreases down the group because oxygen has a strong positive field which attracts the hydroxyl group and removal of H^+ becomes easy.

b) Acidity: Also decreases down the group. Both types of oxides are acidic in nature.

c) SO_2 is a gas whereas SeO_2 is solid. This is because SeO_2 has a chain polymeric structure whereas SO_2 forms discrete units.

3. Reactivity with halogens (Halides):

a) Halides of group 16 are EX_2 EX_4 and EX_6

b) The stability of halides decreases in the order $F^- > Cl^- > Br^- > I^-$. This is because E-X bond length increases with increase in size.

c) Amongst hexahalides only stable halides are SF_6 because of steric reasons which are gaseous and have sp^3d^2 hybridisation and octahedral structure.

d) Amongst tetrafluorides, SF_4 is a gas, SeF_4 a liquid and TeF_4 a solid. These fluorides have sp^3d hybridisation and trigonal bipyramidal structures in which one of the equatorial positions is occupied by a lone pair of electrons. This geometry is also regarded as see-saw geometry.

e) Dihalides are sp^3 hybridised and tetrahedral in shape.

f) Monohalides are dimeric in nature. 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:

$$2Se_2Cl_2 \rightarrow SeCl_4 + 3Se$$

4. Anomalous behaviour of Oxygen: The behaviour of oxygen differs from rest of the elements due to the following reason: It has a small size, it does not have d – orbitals limits, its covalency to four and it has high electronegativity

5. Oxygen:

Preparation:

$$2KClO_3 \xrightarrow{Heat/MnO_2} 2KCl + 3O_2$$

$$2H_2O_2(aq) \xrightarrow{\text{Finely divided metals}} 2H_2O(l) + O_2(g)$$

$$2Ag_2O(s) \xrightarrow{Heat} 4Ag(s) + O_2(g)$$

$$2HgO(s) \xrightarrow{\Delta} 2Hg(l) + O_2(g)$$

$$\underset{\text{Red lead}}{2Pb_3O_4(s)} \xrightarrow{\Delta} 6PbO(s) + O_2(g)$$

$$2PbO_2(s) \xrightarrow{\Delta} 2PbO(s) + O_2(g)$$

Properties:

- Dioxygen is a colourless and odourless gas.
- Oxygen atom has three stable isotopes: ^{16}O, ^{17}O and ^{18}O.

- Molecular oxygen is paramagnetic (by MOT).
- Dioxygen directly reacts with nearly metals and non metals except some noble metals (e.g. Au, Pt) and some noble gases.

6. Oxides: The compounds of oxygen and other elements are called oxide. There are four types:

a. Acidic oxides: Non- metallic oxides are usually acidic in nature.

$$SO_2 + H_2O \longrightarrow H_2SO_3 \text{ (sulphurous acid)}$$

b. Basic oxides: Metallic oxides are mostly basic in nature. Basic oxides dissolve in water forming bases e.g.,

$$Na_2O + H_2O \longrightarrow 2NaOH$$

$$K_2O + H_2O \longrightarrow 2KOH$$

$$CaO + H_2O \longrightarrow Ca(OH)_2$$

c. Amphoteric oxides: They show characteristics of both acidic as well as basic oxides.

$$Al_2O_3 + 6HCl(aq) \longrightarrow 2AlCl_3(aq) + 3H_2O$$

$$Al_2O_3 + 6NaOH(aq) + 3H_2O(l) \longrightarrow 2Na_3[Al(OH)_6](aq)$$

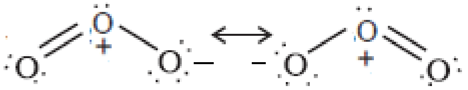
d. Neutral oxides: These oxides are neither acidic nor basic. Example: CO, NO and N_2O

7. Ozone:

Preparation: It is prepared by passing silent electric discharge through pure and dry oxygen. 10 – 15 % oxygen is converted in to ozone.

$$3O_2(g) \longrightarrow 2O_3(g); \qquad \Delta H = +142 \text{ kJ mol}^{-1}$$

Structure of Ozone: Ozone has angular structure. Both O = O bonds are of equal bond length due to resonance.



Properties: Pure ozone is a pale blue gas. It acts as an oxidising agent due to the ease with which it liberates atoms of nascent oxygen ($O_3 \rightarrow O_2 + O$). For example

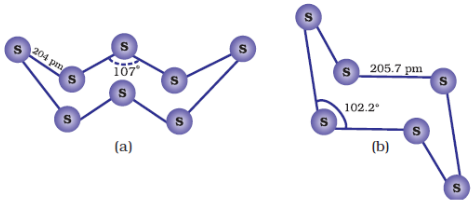
$$PbS(s) + 4O_3(g) \rightarrow PbSO_4(s) + 4O_2(g)$$

$$2I^-(aq) + H_2O(l) + O_3(g) \rightarrow 2OH^-(aq) + I_2(s) + O_2(g)$$

Uses: It is used as a germicide, disinfectant and for sterilising water. It is also used for bleaching oils, ivory, flour, starch, etc.

8. Sulphur:

- Sulphur exhibits most common allotropy is Yellow Rhombic (α - sulphur) and Monoclinic (β- sulphur). At 369 K both forms are stable. It is called transition temperature. Both of them have S_8 molecules. The ring is puckered and has a crown shape.
- Another allotrope of sulphur is – cyclo S_6 form, the ring adopts a chair form.



The structures of (a) S_8 ring in rhombic sulphur and (b) S_6 form

- S_2 is formed at high temperature (~ 1000 K). It is paramagnetic because of 2 unpaired electrons present in anti bonding π* orbitals like O_2

9. Sulphur dioxide (SO_2): The molecule of SO2 is angular. It is a resonance hybrid of the two canonical forms:

Preparation:

- Sulphur dioxide is formed when sulphur is burnt in air or oxygen.

$$S\ (s) + O_2\ (g) \rightarrow SO_2\ (g)$$

- In the laboratory it is generated by treating a sulphite with dilute HCl.

$$NaHSO_3 + HCl \rightarrow NaCl + H_2O + SO_2$$

- Industrially, it is produced as a by-product of the roasting of sulphide ores.

$$4FeS_2\ (s) + 11O_2\ (g) \rightarrow 2Fe_2O_3\ (s) + 8SO_2\ (g)$$

Properties:

- It is color less gas with pungent smell. It is heavier than air and highly soluble in water.
- Sulphur dioxide, when passed through water, forms a solution of sulphurous acid.

$$SO_2\ (g) + H_2O\ (l) \rightarrow H_2SO_3\ (aq)$$

- In the presence of moisture, it liberates nascent hydrogen and thus acts as reducing agent.

$$2Fe^{3+} + SO_2 + 2H_2O \rightarrow 2Fe^{2+} + SO_4^{2-} + 4H^+$$

$$\underset{\text{(Pink violet)}}{5SO_2 + 2MnO_4^-} + 2H_2O \rightarrow 5SO_4^{2-} + 4H^+ + \underset{\text{(colourless)}}{2Mn^{2+}}$$

Here SO_2 turns the pink violet colour of $KMnO_4$ colourless due to reduction of MnO_4 to Mn^{2+}. It is test of presence of SO_2

10. Oxoacids of Sulphur: Sulphur forms a number of oxoacids such as H_2SO_3 (sulphurous acid), H_2SO_4 (sulphuric acid), $H_2S_2O_7$ (pyrosulphuric acid or oleum), $H_2S_2O_8$ (peroxodisulphuric acid).

Sulphuric acid: It is dibasic acid or diprotic acid. Sulphuric acid is very strong acid in water mainly b/c its first ionisation to H_3O^+ and HSO_4^- is large. The second ionisation HSO_4^- to H_3O^+ and SO_4^{2-} is very small so we can say that $Ka_1 >> Ka_2$.

$$H_2SO_4(aq) + H_2O(l) \rightarrow H_3O^+(aq) + HSO_4^-(aq);\ K_{a_1} = \text{very large}\ (K_{a_1} > 10)$$

$$HSO_4^-(aq) + H_2O(l) \rightarrow H_3O^+(aq) + SO_4^{2-}(aq)\ ;\ K_{a_2} = 1.2 \times 10^{-2}$$

Preparation: It is manufactured by the ***Contact process.*** Reaction is exothermic so low temp and high pressure is the favorable conditions for maximum yield. It involves the following steps:

$$S + O_2 \rightarrow SO_2$$

$$SO_2 + O_2 \xrightarrow{V_2O_5} 2SO_3$$

$$SO_3 + H_2SO_4 \rightarrow H_2S_2O_7$$

Oleum is diluted with water to get H_2SO_4 of desired concentration.

$$H_2O + H_2S_2O_7 \rightarrow H_2SO_4$$

Properties: It is a moderately strong oxidizing agent.

It is a strong dehydrating agent.

$$C_{12}H_{22}O_{11} \xrightarrow{H_2SO_4} 12C + 11H_2O$$

GROUP 17: The Halogen Family

A. Atomic and Physical Properties:

1. Outer Electronic Configuration: ns^2np^5

2. Group members: F, Cl, Br, I, At.

3. Atomic and ionic radii: Halogens have the smallest atomic radii in their respective periods because of maximum effective nuclear charge.

4. Oxidation states: All the halogen shows -1 oxidation state. Except fluorine other element also shows +1, +3, +5 and +7.

5. Ionisation enthalpy: They have very high ionization enthalpy in a period but down the group IE decreases.

6. Electron gain enthalpy: Halogens have maximum negative electron gain enthalpy because these elements have only one electron less than stable noble gas configuration. Electron gain enthalpy becomes less negative down the group because atomic size increases down the group.

7. Electronegativity: These elements are highly electronegative in a period but electronegativity decreases down the group. Fluorine is the most electronegative element in the periodic table.

8. Bond dissociation enthalpy: Bond dissociation enthalpy decreases down the group. Bond dissociation enthalpy of Cl_2 is more than F_2 because there are large electronic repulsions of lone pairs present in F_2 so the order of bond dissociation enthalpy is as follow: $Cl_2 > Br_2 > F_2 > I_2$

9. Colour: All halogens are coloured because of absorption of radiations in visible region which results in the excitation of outer electrons to higher energy levels.

10. Oxidising power: All halogens are strong oxidising agents because they have a strong tendency to accept electrons. Order of oxidizing power is $F_2 > Cl_2 > Br_2 > I_2$

B. Chemical Properties of Group 17 Elements:

1. Anomalous behaviour of fluorine: It is due to its small size, highest electronegativity, low F-F bond dissociation enthalpy, and non availability of *d* orbitals in valence shell.

Hydrogen fluoride is a liquid due to strong hydrogen bonding. Other hydrogen halides are gases.

2. Reactivity with H_2:

- **Stability:** HF > HCl > HBr > HI, This is because of decrease in bond dissociation enthalpy.
- **Acidic strength:** HF < HCl < HBr < HI
- **Reducing Strength:** HF < HCl < HBr < HI
- **Boiling point:** As the size increases van der Waals forces increases and hence boiling point increases but HF has strong intermolecular H bonding so order of boiling point is as follow-

  HCl < HBr < HI < HF
- **% Ionic character:** HF > HCl > HBr > HI
- **Dipole moment:** HF > HCl > HBr > HI order is due to electronegativity decreases down the group.

3. Reactivity with metals:

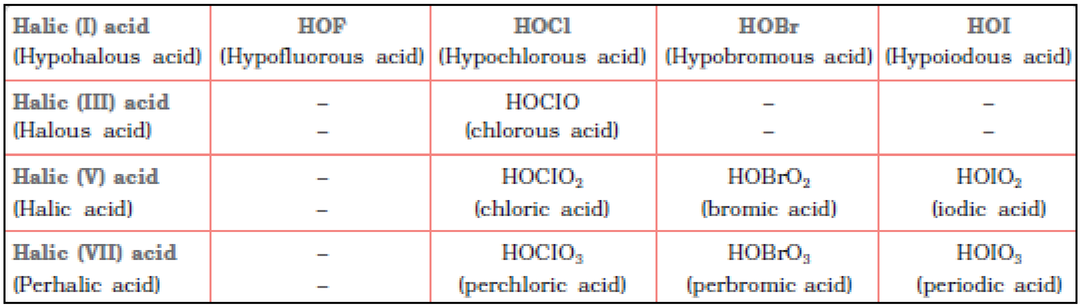
- Halogens react with metals to form halides. In particular metals, ionic character is:

$$M\text{-}F > M\text{-}Cl > M\text{-}Br > M\text{-}I.$$

- Halides in higher oxidation state will be more covalent than the one in the lower oxidation state. For example $SnCl_4 > SnCl_2 > PbCl_4 > PbCl_2$.

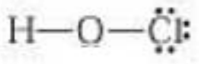
4. Oxoacids of halogens:

- Fluorine forms only one oxo-acid HOF (Fluoric (I) acid or hypofluorous acid) due to high electronegativity. The oxoacids of halogens are as following:

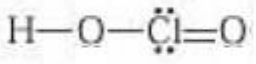


Halic (I) acid (Hypohalous acid)	**HOF** (Hypofluorous acid)	**HOCl** (Hypochlorous acid)	**HOBr** (Hypobromous acid)	**HOI** (Hypoiodous acid)
Halic (III) acid (Halous acid)	– –	$HOClO$ (chlorous acid)	– –	– –
Halic (V) acid (Halic acid)	– –	$HOClO_2$ (chloric acid)	$HOBrO_2$ (bromic acid)	$HOIO_2$ (iodic acid)
Halic (VII) acid (Perhalic acid)	– –	$HOClO_3$ (perchloric acid)	$HOBrO_3$ (perbromic acid)	$HOIO_3$ (periodic acid)

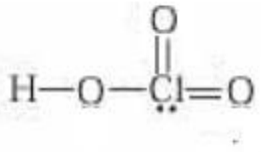
- **Structure of oxoacids of chlorine:**



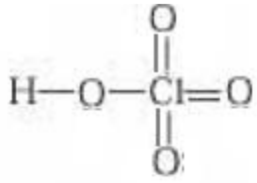
Hypochlorous acid



Chlorous acid



Chloric acid



Perchloric acid

- Acid strength of oxo-acids containing the same halogen are in following order:

$$HOCl < HClO_2 < HClO_3 < HClO_4$$

This is b/c in soln $ClO4^-$ ion is the most stable due to dispersal of –ve charge on four O- atoms or the oxoacids in higher oxidation state is more acidic than that of lower oxidation state

$$HClO_4 \rightarrow H^+ + ClO_4^- \text{ (most stable)}$$

- Acid strength of oxo-acids containing the different halogen are in following order:

$$HOF > HOCl > HOBr > HOI$$

  This is because Fluorine is most electronegative.

5. Interhalogen compounds (Reactivity of halogens towards other halogens): Due to different electronegativity in halogen atoms its combine with each other and to form a number of binary covalent compounds, which are known as interhalogens compounds. These are four types XX', XX'_3, XX'_5 and XX'_7, where X is a larger size halogen than X' and X is more electropositive than X'.

Preparation:

$$\underset{\text{(equal volume)}}{Cl_2 + F_2} \xrightarrow{437\,K} 2ClF; \qquad \underset{\text{(excess)}}{I_2 + 3Cl_2} \rightarrow 2ICl_3$$

$$Cl_2 + \underset{\text{(excess)}}{3F_2} \xrightarrow{573\,K} 2ClF_3; \qquad \underset{\text{(diluted with water)}}{Br_2 + 3F_2} \rightarrow 2BrF_3$$

$$\underset{\text{(equimolar)}}{I_2 + Cl_2} \rightarrow 2ICl; \qquad Br_2 + \underset{\text{(excess)}}{5F_2} \rightarrow 2BrF_5$$

Properties:

- Interhalogen compounds are more reactive than halogens (except F_2) because X-X' is a more polar bond than X-X bond.
- All of these compounds undergo hydrolysis like as: $XX' + H_2O \rightarrow HX' + HOX$
- All are diamagnetic.
- Their melting point is little higher than halogens.
- $:\overset{\cdot\cdot}{\underset{\cdot\cdot}{X}}X'$(like ClF, BrF, BrCl, ICl, IBr, IF) have linear shape, $\overset{\cdot\cdot}{\underset{\cdot\cdot}{X}}X'_3$ (like ClF_3, BrF_3, IF_3, ICl_3) have Bent T- shape, $\overset{\cdot\cdot}{X}X'_5$ (like ClF_5, BrF_5, IF_5) have square pyramidal shape and XX'_7 like IF_7 has pentagonal bipyramidal shape.

Uses: These compounds can be used as non aqueous solvents. Interhalogen compounds are very useful fluorinating agents. ClF_3 and BrF_3 are used for the production of UF_6 in the enrichment of ^{235}U.

$$U(s) + 3ClF_3\,(l) \rightarrow UF_6\,(g) + 3ClF\,(g)$$

6. Chlorine (Cl_2):

Preparation:

i) By heating manganese dioxide with concentrated hydrochloric acid.

$$MnO_2 + 4HCl \rightarrow MnCl_2 + Cl_2 + 2H_2O$$

However, a mixture of common salt and concentrated H2SO4 is also used in place of HCl.

$$4NaCl + MnO_2 + 4H_2SO_4 \rightarrow MnCl_2 + 4NaHSO_4 + 2H_2O + Cl_2$$

ii) By the action of HCl on potassium permanganate.

$$2KMnO_4 + 16HCl \rightarrow 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2$$

Manufacture of Chlorine:

i) Deacon's process: By oxidation of HCl gas by atmospheric oxygen in the presence of $CuCl_2$ (catalyst) at 723 K.

$$4HCl + O_2 \rightarrow Cl_2 + 2H_2O$$

ii) Electrolytic process: Chlorine is obtained by the electrolysis of brine solution (concentrated NaCl solution). Chlorine is liberated at anode.

$$\text{At cathode: } NaCl\,(aq) \rightarrow Na^+\,(aq) + Cl^-\,(aq)$$

$$\text{At anode: } 2Cl^- \rightarrow Cl_2 + 2e^-$$

Properties: It is a greenish yellow gas with pungent and suffocating odour. It is about 2-5 times heavier than air. It is soluble in water.

i) Chlorine reacts with a number of metals and non-metals to form chlorides.

$$2Al + 3Cl_2 \rightarrow 2AlCl_3; \qquad P4 + 6Cl_2 \rightarrow 4PCl_3$$

$$2Na + Cl_2 \rightarrow 2NaCl; \qquad S8 + 4Cl_2 \rightarrow 4S2Cl_2$$

ii) It has great affinity for hydrogen. It reacts with compounds containing hydrogen to form HCl.

$$H_2 + Cl_2 \rightarrow 2HCl$$
$$H_2S + Cl_2 \rightarrow 2HCl + S$$

iii) With excess ammonia, chlorine gives nitrogen and ammonium chloride where as with excess chlorine; nitrogen trichloride (explosive) is formed.

$$\underset{\text{(excess)}}{8NH_3} + 3Cl_2 \rightarrow 6NH_4Cl + N_2; \qquad NH_3 + \underset{\text{(excess)}}{3Cl_2} \rightarrow NCl_3 + 3HCl$$

iv) With cold and dilute alkalies produces a mixture of chloride and hypochlorite but with hot and concentrated alkalies it gives chloride and chlorate. It is an example of disproportion reaction.

$$2NaOH + Cl_2 \rightarrow NaCl + NaOCl + H_2O; \quad \text{(cold and dilute)}$$
$$6NaOH + 3Cl_2 \rightarrow 5NaCl + NaClO_3 + 3H_2O \quad \text{(hot and conc.)}$$

v) With dry slaked lime it gives bleaching powder.

$$2Ca(OH)_2 + 2Cl_2 \rightarrow Ca(OCl)_2 + CaCl_2 + 2H_2O$$

The composition of bleaching powder is $Ca(OCl)_2.CaCl_2.Ca(OH)_2.2H_2O$.

vi) Oxidising and bleaching properties: Chlorine dissolves in water to give HCl and HOCl (hypochlorus acid). Formed HOCl gives nascent oxygen which is responsible for oxidising and bleaching properties of chlorine.

- So it's a powerful bleaching agent and the bleaching action is due to oxidation.

  $$Cl_2 + H_2O \rightarrow 2HCl + O$$
  $$\text{Coloured substance} + O \rightarrow \text{Colourless substance}$$

- It oxidises ferrous to ferric, sulphite to sulphate, sulphur dioxide to sulphuric acid and iodine to iodic acid.

$$2FeSO_4 + H_2SO_4 + Cl_2 \rightarrow Fe_2(SO_4)_3 + 2HCl$$
$$Na_2SO_3 + Cl_2 + H_2O \rightarrow Na_2SO_4 + 2HCl$$
$$SO_2 + 2H_2O + Cl_2 \rightarrow H_2SO_4 + 2HCl$$
$$I_2 + 6H_2O + 5Cl_2 \rightarrow 2HIO_3 + 10HCl$$

Uses:

i) Used for bleaching wood pulp, cotton and textiles.

ii) In the extraction of gold and platinum.

iii) In sterilizing drinking water.

iv) Preparation of poisonous gases such as phosgene ($COCl_2$), tear gas (CCl_3NO_2), mustard gas ($ClCH_2CH_2SCH_2CH_2Cl$).

7. Hydrogen Chloride (HCl):

Preparation: In laboratory, it is prepared by heating sodium chloride with concentrated sulphuric acid. HCl gas can be dried by passing through concentrated sulphuric acid.

$$NaCl + H_2SO_4 \xrightarrow{420\,K} NaHSO_4 + HCl$$
$$NaHSO_4 + NaCl \xrightarrow{823\,K} Na_2SO_4 + HCl$$

Properties: It is a colourless and pungent smelling gas. It is extremely soluble in water. Its aqueous solution is called hydrochloric acid.

i) It reacts with ammonia and gives white fumes of ammonium chloride.

$$NH_3 + HCl \rightarrow NH_4Cl$$

ii) When three parts of concentrated HCl and one part of concentrated HNO3 are mixed, aqua regia is formed which is used for dissolving noble metals, e.g., gold, platinum.

$$Au + 4H^+ + NO_3^- + 4Cl^- \rightarrow AuCl_4^- + NO + 2H_2O$$

$$3Pt + 16H^+ + 4NO_3^- + 18Cl^- \rightarrow 3PtCl_6^{2-} + 4NO + 8H_2O$$

iii) Hydrochloric acid decomposes salts of weaker acids, like

$$Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2O + CO_2$$

$$NaHCO_3 + HCl \rightarrow NaCl + H_2O + CO_2$$

$$Na_2SO_3 + 2HCl \rightarrow 2NaCl + H_2O + SO_2$$

Uses:

i) It is used for extracting glue from bones and purifying bone black

ii) In medicine and as a laboratory reagent.

GROUP 18 (ZERO GROUP): Noble Gases

A. Atomic and Physical Properties: All the noble gases are colorless, tasteless mono-atomic and sparingly soluble in water.

1. Outer Electronic Configuration: ns^2np^6

2. Group members: He, Ne, Ar, Kr, Xe and Rn.

3. Ionisation enthalpy: They have very high IE b/c of completely filled orbitals.

4. Electron gain enthalpy: They have large positive value of electron gain enthalpy because of stable electronic configuration.

5. Melting and boiling point: Low melting and boiling point b/c noble gases being monoatomic have no inter atomic forces except weak dispersion forces and therefore, they are liquefied at very low temperatures. Hence, they have low boiling points. Helium has the lowest boiling point (4.2 K) of any known substance. It is increases down the group.

B. Chemical Properties: In general, noble gases are least reactive. Their inertness to chemical reactivity is attributed to the following reasons:

(i) The noble gases except helium ($1s^2$) have completely filled ns^2np^6 electronic configuration in their valence shell.

(ii) They have high ionisation enthalpy and more positive electron gain enthalpy.

1. Compounds of Xe and F:

i) Xenon forms three binary fluorides, XeF2, XeF4 and XeF6 by the direct reaction of elements under appropriate experimental conditions.

$$\underset{\text{(xenon in excess)}}{Xe(g) + F_2(g)} \xrightarrow{673\text{ K},\ 1\text{ bar}} XeF_2(s)$$

$$\underset{\text{(1:5 ratio)}}{Xe(g) + 2F_2(g)} \xrightarrow{873\text{ K},\ 7\text{ bar}} XeF_4(s)$$

$$\underset{\text{(1:20 ratio)}}{Xe(g) + 3F_2(g)} \xrightarrow{573\text{ K},\ 60\text{–}70\text{bar}} XeF_6(s)$$

ii) XeF_6 can also be prepared by the interaction of XeF_4 and O_2F_2 at 143K.

$$XeF_4 + O_2F_2 \rightarrow XeF_6 + O_2$$

Properties:

i) XeF_2, XeF_4 and XeF_6 are colourless crystalline solids. They are powerful fluorinating agents. They are readily hydrolysed even by traces of water like

$$2XeF_2\ (s) + 2H_2O(l) \rightarrow 2Xe\ (g) + 4\ HF(aq) + O_2(g)$$

ii) Xenon fluorides react with fluoride ion acceptors to form cationic species and fluoride ion donors to form fluoro anions.

$$XeF_2 + PF_5 \rightarrow [XeF]^+\ [PF_6]^-; \quad XeF_4 + SbF_5 \rightarrow [XeF_3]^+\ [SbF_6]^-$$

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

2. Compounds of Xe and O:

i) Hydrolysis of XeF_4 and XeF_6 with water gives XeO_3.

$$6XeF_4 + 12\ H_2O \rightarrow 4Xe + 2Xe0_3 + 24\ HF + 3\,O_2$$

$$XeF_6 + 3\ H_2O \rightarrow XeO_3 + 6\ HF$$

ii) Partial hydrolysis of XeF_6 gives oxyfluorides like xenon oxytetrafluoride ($XeOF_4$) and xenon dioxydifluoride (XeO_2F_2).

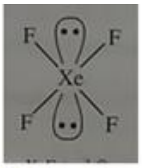
$$XeF_6 + H_2O \rightarrow XeOF_4 + 2\ HF$$

$$XeF_6 + 2\ H_2O \rightarrow XeO_2F_2 + 4HF$$

Properties: XeO3 is a colourless explosive solid and has a pyramidal molecular structure (Fig. 7.9). XeOF4 is a colourless volatile liquid and has a square pyramidal molecular structure (Fig.7.9).

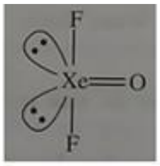
3. Structure of Xenon compounds:

XeF_2 (sp^3d)
Linear

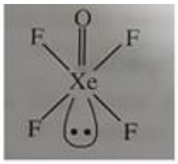


XeF_4 (sp^3d^2)
Square planar

XeF_6 (sp^3d^3)
Distorted octahedral



$XeOF_2$ (sp^3d)
T-shaped



$XeOF_4$ (sp^3d^2)
Square pyramidal

XeO_3 (sp^3)
Trigonal pyramidal

4. Uses:

i) Helium is a non-inflammable and light gas. Hence, it is used in filling balloons for meteorological observations.

ii) It is also used in gas-cooled nuclear reactors.

iii) Liquid helium (b.p. 4.2 K) finds use as cryogenic agent.

iv) It is used to produce and sustain powerful superconducting magnets.

v) Neon is used in discharge tubes and fluorescent bulbs for advertisement display purposes.

vi) Argon is used mainly to provide an inert atmosphere in high temperature metallurgical processes (arc welding of metals or alloys) and for filling electric bulbs.

vii) There are no significant uses of Xenon and Krypton. They are used in light bulbs designed for special purposes.