p-BLOCK ELEMENTS

GROUP 15 ELEMENTS : THE NITROGEN FAMILY

Group 15 includes nitrogen phosphorus, arsenic, antimony and bismuth. As we go down the group, there is a shift from non-metallic to metallic through metalloidic character. Nitrogen and phosphorus are non-metal, arsenic and antimony metalloid and bismuth is a typical metal.

Electronic Configuration :

The valence shell electronic configuration of these element is ns^2 np^3 the s orbital in these element is completely filled and p orbitals are half- filled, making their electronic configuration extra stable.

Atomic and Ionic Radii :

Covalent and ionic (in a particular state) radii increase in size down the group. There is a considerable increase in covalent radius from N to P. However, from As to Bi only a small increase in covalent radius is observed. This is due to the presence of completely filled d and / or f orbitals in heavier members.

Ionisation Enthalpy:

Ionisation enthalpy decreases down the group due to gradual increase in atomic size. Because of the extra stable half- filled p-orbital electronic configuration and smaller size, the ionisation enthaply of the group 15 element is much greater than of group 14 elements in the corresponding periods. The order of successive ionisation enthalpies, as expected is $\Delta_i H_1 < \Delta_i H_2 < \Delta_i H_3$

Electronegativity :

The electronegativity value, in general, decreases down the group with increasing atomic size. However, amongst the heavier elements, the difference is not that much pronounced.

Physical Properties:

All the elements of this group are polyatomic. Dinitrogen is a diatomic gas while all others are solids. Metallic character increases down the group. Nitrogen and phosphours are non – metals , arsenic and antimony metalloids and bismuth is a metal. This is due to decrease in ionisation enthalpy and increase in atomic size. The boiling points , in general , increase from top to bottom in the group but the melting point increases upto arsenic and then decreases upto bismuth. Except nitrogen , all the elements show allotropy.

ATOMIC & PHYSICAL PROPERTIES

Element		N	P	As	Sb	Bi
Atomic Number		7	15	33	51	83
Atomic Mass		14.01	30.97	74.92	121.76	208.98
Electronic configuration		[He] $2s^2$ $2p^3$	[Ne] $3s^2$ $3p^3$	[Ar] $3d^{10}$ $4s^2$ $4p^3$	[Kr] $4d^{10}$ $5s^2$ $5p^3$	[Xe] $4f^{14}$ $5d^{10}$ $6s^2$ $6p^3$
Covalent Radius / pm		70	110	120	140	150
Ionic Radius / pm **a = M^{3-}, b = M^{+3}**		171^a	212^a	222^a	76^b	103^b
Ionization enthalpy / (kJ mol^{-1})	I	1402	1012	947	834	703
	II	2856	1903	1798	1595	1610
	III	4577	2910	2736	2443	2466
Electronegativity		3.0	2.1	2.0	1.9	1.9

Chemical Properties :

Oxidation States and trends in a chemical reactivity :

The common oxidation states of these elements are – 3 , + 3 and + 5. The tendency to exhibit – 3 oxidation state decreases down the group , bismuth hardly forms any compound in –3 oxidation state. The stability of + 5 oxidation state decreases down the group. The only well characterised Bi (V) compound is BiF_5 .The stability of + 5 oxidation state decreases and that of +3 state increases (due to inert pair effect) down the group. Nitrogen exhibits +1 , + 2 , + 4 oxidation states also when it reacts with oxygen. Phosphours also shows + 1 and + 4 oxidation states in some oxoacids.

In the case of nitrogen , all oxidation states from +1 to +4 tend to disproportionate in acid solution. For example ,

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

Similarly , in case of phosphorus nearly all intermediate oxidation states disproportionate into +5 and –3 both in alkali and acid. However +3 oxidation state in case of arsenic , antimony and bismuth become increasingly stable with respect to disproportionation.

Nitrogen is restricted to a maximum covalency of 4 since only four (one s and three p) orbitals are available for bonding. The heavier elements have vacant d orbitals in the outermost shell which can be used for bonding (covalency) and hence , expand their covalence as in PF_6^- .

Anomalous properties of nitrogen :

Nitrogen differs from the rest of the members of this group due to its smaller size , high electronegativity , high ionisation enthalpy and non – availability of d orbitals. Nitrogen has unique ability to form $p\pi - p\pi$ multiple bonds with itself and with other elements having small size and high electronegativity (e.g., C ,O). Heavier elements of this group do not form $p\pi - p\pi$ bonds as their atomic orbitals are so large and diffuse that they cannot have effective overlapping. Thus, nitrogen exists as a diatomic molecule with a triple bond (one s and two p) between the two atoms. Consequently , its bond enthalpy (941.1 kJ mol^{-1}) is very high. On the contrary , phosphorus , arsenic and antimony form metallic bonds in elemental state. However , the single N – N bond is weaker than the single P – P bond because of high interelectronic repulsion of the non – bonding electrons , owing to the small bond length. As a result the catenation tendency is weaker in nitrogen. Another factor which affects the chemistry of nitrogen is the absence of d orbitals in its valence shell. Besides restricting its covalency to four , nitrogen cannot form $d\pi - p\pi$ bonds as the heavier elements can e.g., $R_3P = O$ or $R_3P = CH_2$ (R = alkyl group). Phosphours and arsenic can form $d\pi - p\pi$ bond also with transition metals when their compounds like $P(C_2H_5)_3$ and $As(C_6H_5)_3$ act as ligands.

(i) Reactivity towards hydrogen :

All the elements of Group 15 form hydrides of the type EH_3 where E = N , P, As, Sb or Bi. Some of the properties of these hydrides are shown in Table. The hydrides show regular gradation in their properties. The stability of hydrides decreases from NH_3 to BiH_3 which can be observed from their bond dissociation enthalpy. Consequently , the reducing character of the hydrides increases. Ammonia is only a mild reducing agent while BiH_3 is the strongest reducing agent amongst all the hydrides. Basicity also decreases in the order

$$NH_3 > PH_3 > AsH_3 > SbH_3 \geq BiH_3 .$$

Properties of Hydrides of Group 15 Elements

Property	**NH_3**	**PH_3**	**AsH_3**	**SbH_3**	**BiH_3**
Melting point / K	195.2	139.5	156.7	185	–
Boiling point / K	238.5	185.5	210.6	254.6	290
(E – H) Distance / pm	101.7	141.9	151.9	170.7	–
HEH angle (^{0})	107.8	93.6	91.8	91.3	–
$\Delta_f H^- / kJ\ mol^{-1}$	– 46.1	13.4	66.4	145.1	278
$\Delta_{diss} H^-(E – H) / kJ\ mol^{-1}$	389	322	297	255	–

(ii) Reactivity towards oxygen :

All these elements form two types of oxides : E_2O_3 and E_2O_5 . The oxide in the higher oxidation state of the element is more acidic than that of lower oxidation state. Their acidic character decreases down the group. The oxides of the type E_2O_3 of nitrogen and phosphours are purely acidic , that of arsenic and antimony amphoteric and those of bismuth is predominantly basic.

(iii) Reactivity towards halogens :

These elements react to form two series of halides : EX_3 and EX_5 . Nitrogen does not form pentahalide due to non – availability of the d – orbitals in its valence shell. Pentahalides are more covalent than trihalides. All the trihalides of these elements except those of nitrogen are stable. In case of nitrogen , only NF_3 is known to be stable. Trihalides except BiF_3 are predominantly covalent in nature.

(iv) Reactivity towards metals :

These elements react with metals to form their binary compounds exhibiting –3 oxidation state , such as , Ca_3N_2 (calcium nitride) Ca_3P_2 (calcium phosphide) , Na_3As_2 (sodium arsenide) , Zn_3Sb_2 (zinc antimonide) and Mg_3Bi_2 (magnesium bismuthide).

- **NITROGEN (N):**

❍ **PREPARATION:**

(i) By heating a mixture of NH_4Cl and $NaNO_2$. N_2 is collected by the downward displacement of water.

$NH_4Cl + NaNO_2 \xrightarrow{\Delta} NH_4NO_2 + NaCl$; $NH_4NO_2 \xrightarrow{\Delta} N_2\uparrow + 2H_2O$

* By treating an aqueous solution of ammonium chloride with sodium nitrate. It is laboratory method of preparation.

$NH_4Cl(aq) + NaNO_2(aq) \longrightarrow N_2(g) + H_2O\ (\ell) + NaCl_{(aq)}$

(ii) By heating ammonium dichromate:

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

(iii) By oxidation of ammonia

(A) At lower temperature

(a) $8NH_3\ (\ell) + 3Cl_2\ (g) \longrightarrow 6NH_4Cl + N_2\uparrow$

If excess of Cl_2 is used in this reaction, nitrogen trichloride is formed as per the following reaction,

$NH_3 + 3Cl_2 \longrightarrow NCl_3 + 3HCl$

Nitrogen trichloride is an explosive substance.

(b) By reation of ammonia with calcium hypochlorite or Br_2

$4NH_3 + 3Ca(OCI)_2 \longrightarrow 3CaCl_2 + N_2 + H_2O$

(B) At higher temperature

By passing ammonia over heated cupric oxide or PbO :

$2NH_3 + 3CuO \longrightarrow N_2\uparrow + 3Cu + 3H_2O$

(iv) By heating urea with a nitrite in presence of dilute H_2SO_4:

$NH_2CONH_2 + 2NaNO_2 + H_2SO_4 \xrightarrow{\Delta} Na_2SO_4 + 2N_2\uparrow + 3H_2O + CO_2\uparrow$

(v) By heating urea solution with sodium hypobromite:

$NH_2CONH_2 + 3NaOBr \xrightarrow{\Delta} N_2\uparrow + 3NaBr + 2H_2O + CO_2\uparrow$

(vi) By passing nitric oxide and NH_3 over red hot copper gauze:

$4NH_3 + 6NO \longrightarrow 5N_2\uparrow + 6H_2O$

(vii) By passing HNO_3 vapours on red hot copper:

$5Cu + 2HNO_3 \longrightarrow 5CuO + N_2\uparrow + H_2O$

(viii) Very pure nitrogen ; $Ba(N_3)_2 \xrightarrow{\Delta} Ba + 3N_2$

Sodium azide also gives N_2 on heating.

INDUSTRIAL METHODS OF PREPARATION:

(i) From liquefied air by fractional distillation : The bp of N_2 is –196°C and that of oxygen is –183°C and hence they can be separated.

(ii) From producer gas from furnaces : Producer gas is a mixture of CO and N_2. When the mixture of CO and N_2 is passed over heated CuO, the CO gas is oxidized to CO_2 which is absorbed in alkalies & N_2 remains which is collected in gas cylinders.

❍ **PROPERTIES:**

(i) N_2 is a colourless, odourless gas insoluble in water.

(ii) It is non-polar covalent and neutral molecule.

(iii) It is neither combustible nor a supporter of combustion.

(iv) It is absorbed by heated Mg and Al. The nitrides formed thus react with water to form NH_3.

$3Mg + N_2 \longrightarrow Mg_3N_2\ (+\ 6H_2O) \longrightarrow 3Mg(OH)_3 + 2NH_3\uparrow$

$2Al + N_2 \longrightarrow 2AlN\ (+\ 6H_2O) \longrightarrow 2Al(OH)_3 + 2NH_3\uparrow$

(v) Reaction with H_2: At 200 atm and 500°C, and in the presence of iron catalyst and molybdenum promoter, N_2 combines with H_2 reversibly to form ammonia. The process is called Haber’s Process and is the industrial method of manufacturing ammonia. The reaction is exothermic.

$N_2 + 3H_2 \longrightarrow 2NH_3$

(vi) Reaction with oxygen: When air free from CO_2 and moisture is passed over an electric arc at about 2000 K, nitric oxide is formed. This reaction is endothermic.

$$N_2 + O_2 \longrightarrow 2NO$$

(vii) Reaction with CaC_2 and BaC_2: At 1100°C, these carbides react with N_2 forming $CaCN_2$ and $Ba(CN)_2$ respectively.

$CaC_2 + N_2 + \xrightarrow{\Delta} CaCN_2 + C$ (nitrolim, a fertilizer) ; $BaC_2 + N_2 + \xrightarrow{\Delta} Ba(CN)_2$

$CaCN_2$ reacts with H_2O in the soil to produce NH_3 gas. NH_3 gas is converted by the nitrating bacteria present in soil into nitrates. (The nitrates are readily absorbed by the plants and meet their requirement of the element nitrogen.)

❍ **USES :**

(i) for providing an inert atmosphere during many industrial processes where presence of air or O_2 is to be avoided.

(ii) for manufacture of NH_3 by the Haber's process.

(iii) for manufacture of HNO_3 by the Birkeland-Eyde process.

(iv) for manufacture of nitrolim.

● **COMPOUNDS OF NITROGEN :**

❍ **AMMONIA :**

❍ **PREPARATION :**

(i) By the action of any base or alkali on any ammonium salt :

$NH_4Cl + NaOH \xrightarrow{\Delta} NH_3\uparrow + NaCl + H_2O$; $(NH_4)_2SO_4 + 2NaOH \xrightarrow{\Delta} 2NH_3\uparrow + Na_2SO_4 + 2H_2O$

$NH_4NO_3 + NaOH \xrightarrow{\Delta} NH_3\uparrow + NaNO_3 + H_2O$; $(NH_4)_3PO_4 + 3NaOH \xrightarrow{\Delta} 3NH_3\uparrow + Na_3PO_4 + 3H_2O$

$(NH_4)_2SO_4 + CaO \xrightarrow{\Delta} 2NH_3\uparrow + CaSO_4 + H_2O$

This is a general method and is used as a test for ammonium salts.

(ii) By the hydrolsis of metal nitrides like AlN or Mg_3N_2.

$AlN + NaOH + H_2O \longrightarrow NaAlO_2 + NH_3$

(iii) From oxides of nitrogen: When oxides of nitrogen are mixed with H_2 and the mixture is passed over heated platinum catalyst, NH_3 gas is evolved.

$2NO + 5H_2 \longrightarrow 2NH_3\uparrow + 2H_2O$;$2NO_2 + 7H_2 \longrightarrow 2NH_3\uparrow + 4H_2O$

(iv) From organic amides: When an organic amide is heated with NaOH solution ammonia is evolved.

$CH_3CONH_2 + NaOH \xrightarrow{\Delta} CH_3COONa + NH_3\uparrow$

(v) From nitrates and nitrites: When a metal nitrate or nitrite is heated with zinc powder and concentrated NaOH solution ammonia is obtained. The reactions are

$NaNO_3 + 7NaOH + 4Zn \longrightarrow 4Na_2ZnO_2 + NH_3\uparrow + 2H_2O$

$NaNO_2 + 3Zn + 5NaOH \longrightarrow 3Na_2ZnO_2 + H_2O + NH_3\uparrow$

Thus a nitrite or a nitrate can be identified by this reaction but this test cannot make distinction between them.

☞ The ammonia evolved is passed through quick lime to dry it and collected by the downward displacement of air. Ammonia cannot be dried using $CaCl_2$, P_2O_5, or conc. H_2SO_4 because NH_3 reacts with all of these.

$CaCl_2 + 8NH_3 \longrightarrow CaCl_2 \cdot 8NH_3$; $P_2O_5 + 6NH_3 + 3H_2O \longrightarrow 2(NH_4)_3PO_4$

$H_2SO_4 + 2NH_3 \longrightarrow (NH_4)_2SO_4$

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

INDUSTRIAL METHODS OF PREPARATION:

(i) Haber's process : $N_2 + 3H_2 \xrightarrow[\text{Iron oxide}+K_2O\,\&\,Al_2O_3]{500^\circ C,\ 200\,atm.} 2NH_3$

(ii) From destructive distillation of coal: When coal is heated at a high temperature in an iron retort and the distillate is bubbles in water, three substances are obtained:

(a) Tarry black pitch, (b) Liquor ammonia & (c) Coal gas

The liquor ammonia is a concentrated solution of ammonia and ammonium salts. When heated it gives out ammonia. When all the free NH_3 is obtained, the residual liquid is heated with $Ca(OH)_2$ when ammonium salts get decomposed to liberate further quantity of ammonia.

(iii) Cyanamide process: $CaO + 2C + N_2 \xrightarrow{2000^\circ C} CaCN_2 + CO\uparrow$; $CaCN_2 + 3H_2O \longrightarrow CaCO_3 + 2NH_3\uparrow$

PROPERTIES:

(i) Colourless gas lighter than air. Being basic in nature turns red litmus blue. It acts as a Lewis base

(ii) Highly soluble in water. The solution is called ammonium hydroxide solution.

(iii) $Na + NH_3 \xrightarrow{\Delta} NaNH_2 + 1/2\ H_2$

Amides decompose back with water to form NH_3 and NaOH.

(iv) $4NH_3 + 5O_2 \xrightarrow{Pt,\,550^\circ C} 4NO + 6H_2O$ (Ostwald's process of manufacturing HNO_3)

(v) When Cl_2 is bubbled in liquor ammonia, nitrogen gas is formed.

$$8NH_3 + 3Cl_2 \longrightarrow 6NH_4Cl + N_2\uparrow$$

With excess of Cl_2 it is converted to an explosive substance, nitrogen trichloride.

$$NH_3 + 3Cl_2 \longrightarrow NCl_3 + 3HCl$$

(vi) Cupric oxide and PbO are reduced to metal when NH_3 is passed over heated CuO and PbO.

$3CuO + 2NH_3 \longrightarrow 3Cu + 3H_2O + N_2\uparrow$; $3PbO + 2NH_3 \longrightarrow 3Pb + 3H_2O + N_2\uparrow$

(vii) $CuSO_4 + 2NH_4OH \longrightarrow Cu(OH)_2\downarrow(\text{blue}) + (NH_4)_2SO_4$

$Cu(OH)_2 + (NH_4)_2SO_4 + 3NH_4OH\ (\text{excess}) \longrightarrow [Cu(NH_3)_4]SO_4\ (\text{deep blue solution}) + 4H_2O$

$ZnSO_4 + 2NH_4OH \longrightarrow Zn(OH)_2\downarrow\ (\text{white}) + (NH_4)_2SO_4$

$Zn(OH)_2 + (NH_4)_2SO_4 + 2NH_4OH\ (\text{excess}) \longrightarrow [Zn(NH_3)_4]\ SO_4\ (\text{colourless solution}) + 4H_2O$

Similar reactions occur with $CdSO_4$ solution also.

(viii) $M(NO_3)_2 + 2NH_4OH \longrightarrow M(OH)_2\downarrow\ (\text{white}) + 2NH_4NO_3$

$MCl_2 + 2NH_4OH \longrightarrow M(OH)_2\downarrow\ (\text{white}) + 2NH_4Cl$

(M = Mg, Ca, Sr, Ba, Ra, Sn, Pb)

(ix) When NH_4OH solution is added to $AgNO_3$ solution, a brown ppt. is obtained

$$2AgNO_3 + 2NH_4OH \longrightarrow Ag_2O\downarrow\ (\text{brown}) + 2NH_4NO_3 + H_2O$$

☞ Brown ppt of silver oxide formed dissolves in excess ammonium hydroxide forming a soluble complex

$$Ag_2O + 2NH_4OH \longrightarrow [Ag(NH_3)_2]OH\ (\text{colourless solution}) + 2H_2O$$

Similarly with mercuric salts, NH_4OH forms a white precipitate

$$HgCl_2\ (\text{aq.}) + 2NH_4OH \longrightarrow HgNH_2Cl\downarrow\ (\text{white}) + NH_4Cl + H_2O$$

(x) When liquor ammonia is dropped on heated bleaching powder, nitrogen gas is formed

$$3Ca(OCl)Cl + 2NH_3 \longrightarrow 3CaCl_2 + 3H_2O + N_2\uparrow$$

(xi) $2NH_3 + CO_2 + H_2O \longrightarrow (NH_4)_2CO_3$; $2NH_3 + CO_2 \xrightarrow[\Delta]{\text{high pressure}} NH_2CONH_2\ (\text{urea}) + H_2O$

(xii) When NH_3 gas is passed into the colourless solution of Nessler's reagent a brown precipitate or coloration is formed. This is a test for NH_3 gas.

$$2K_2HgI_4 + 3KOH + NH_3 \longrightarrow H_2N\cdot HgO\cdot HgI\downarrow\ (\text{brown}) + 7KI + 2H_2O$$

(xiii) $H_2PtCl_6 + 2NH_4Cl \longrightarrow (NH_4)_2\ [PtCl_6]\downarrow$ yellow + 2HCl

USES: (i) Used as a refrigeration fluid. (ii) For the production of ammonium fertilizers such as ammonium sulphate, ammonium phosphate, ammonium nitrate, urea etc. (iii) For removing grease because NH_4OH dissolves grease. (iv) For manufacture of HNO_3 by the Ostwald process. (v) As a laboratory reagent. (vi) In the production of artificial rayon, silk, nylon etc.

(2) OXIDES OF NITROGEN :

Nitrogen forms a number of oxides, N_2O, NO, N_2O_3, NO_2 or N_2O_4 and N_2O_5, and also very unstable NO_3 and N_2O_6. All these oxides of nitrogen exhibit *p*®-*p*® multiple bonding between nitrogen and oxygen.

Name	Formula	Colour	Remarks
Nitrous oxide	N_2O	Colourless (g)	Neutral ,+ 1 oxidation state
Nitric oxide	NO	Colourless (g)	Neutral ,+ 2 oxidation state
Dinitrogen trioxide	N_2O_3	Dark blue (s)	Acidic ,+ 3 oxidation state
Nitrogen dioxide	NO_2	Brown (g)	Acidic , + 4 oxidation state
Dinitrogen tetroxide	N_2O_4	Colourless (s)	Extensively dissociated to NO_2 as gas and partly dissociated as liquid, acidic, + 4 oxidation state
Dinitrogen pentoxide	N_2O_5	Colourless (s)	Unstable as gas; ionic solid NO^+_2, NO_3^-, acidic, +5 oxidation state

PREPARATION :

(i) N_2O is obtained generally by heating NH_4NO_3 with caution.

$$NH_4NO_3 \longrightarrow N_2O + 2H_2O \quad ; \quad 2NO + H_2SO_3 \longrightarrow N_2O + H_2SO_4$$

(ii) NO is best prepared by the reduction of 8 M HNO_3 with reducing agents like Cu or by reduction of nitrous acid or nitrites by Fe^{2+} or I^- ions.

$$3Cu + 8HNO_3 \longrightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$$

$$2NaNO_2 + 2FeSO_4 + 3H_2SO_4 \longrightarrow 2NaHSO_4 + Fe_2(SO_4)_3 + 2NO + 2H_2O$$

$$2NaNO_2 + 2NaI + 4H_2SO_4 \longrightarrow 4NaHSO_4 + 2NO + I_2 + 2H_2O$$

(iii) N_2O_3 is obtained as an intense blue liquid or a pale blue solid on cooling an equimolar mixture of NO and NO_2 to 250 K.

$$NO + NO_2 \longrightarrow N_2O_3$$

On warming, its colour fades due to its dissociation into these two oxides.

(iv) NO_2 can be prepared by reduction of concentrated HNO_3 with Cu or by heating heavy metal nitrates.

$$Cu + 4HNO_3 \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O \; ; \quad 2Pb(NO_3)_2 \xrightarrow{673K} 2PbO + 4NO_2 + O_2$$

(v) N_2O_5 is an anhydride of HNO_3. It is best prepared by dehydrating HNO_3 by P_4O_{10} at low temperatures.

$$4HNO_3 + P_4O_{10} \xrightarrow{250K} 2N_2O_5 + 4HPO_3$$

PROPERTIES:

Oxides of nitrogen are all oxidizing agents, N_2O even supporting the combustion of S and P. NO which is thermally more stable, supports the combustion of Mg and P but not of S. Sulphur flame is not hot enough to decompose it.

N_2O is isoelectronic with CO_2 and also has a linear structure. However, unlike CO_2, N_2O has a small dipole moment.

NO has a total of 15 electrons. It is impossible for all of them to be paired and hence this is an odd electron molecule. In the gaseous state, it is paramagnetic. However, the liquid and the solid states are diamagnetic because loose dimmers are formed canceling out the magnetic effects of unpaired electrons.

The brown ring formed in the test for nitrates is due to the formation of a complex of iron, $[Fe(H_2O)_5NO]^{2+}$.

NO_2 with 23 electrons is again an odd electron molecule. In the gaseous state it is paramagnetic. On cooling, the gas condenses to a brown liquid and eventually to a colourless solid both of which are diamagnetic due to dimerisation.

Liquid N_2O_4 undergoes self-ionization to form NO^+ and NO_3^- ions and therefore, it has been extensively studied as a non-aqueous solvent.

☞ N_2O : (a) Reduction : $Cu(hot) + N_2O \longrightarrow CuO + N_2$

(b) Oxidation : $2KMnO_4 + 3H_2SO_4 + 5N_2O \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 10NO$

(c) Supporter of combustion : $Mg + N_2O \longrightarrow MgO + N_2$

☞ NO : (a) Supporter of combustion : $S + 2NO \longrightarrow SO_2 + N_2$

(b) Oxidising properties (Reduction of NO) :

$5H_2 + 2NO \xrightarrow{\text{Pt-black}} 2NH_3 + 2H_2O$

$SO_2 + H_2O + 2NO \longrightarrow H_2SO_4 + N_2O$

$H_2S + 2NO \longrightarrow H_2O + N_2O + S$

(c) Reducing properties (oxidation of NO) :

$2NO + X_2 \longrightarrow 2NOX$

$6KMnO_4 + 9H_2SO_4 + 10NO \longrightarrow 3K_2SO_4 + 6MnSO_4 + 4H_2O + 10HNO_3$

☞ N_2O_3 : (a) $N_2O_3 + KOH \longrightarrow 2KNO_2 + H_2O$

(b) It is anhydride of HNO_2 :

$2HNO_2 \longrightarrow N_2O_3 + H_2O$

(c) with concentrated acids, form nitrosyl salts

$N_2O_3 + 2HClO_4 \longrightarrow 2NO[CIO_4] + H_2O$

☞ NO_2 : It behaves both like HNO_2 and HNO_3. It behaves like HNO_2 as a reducing agent and like HNO_3 as an oxidising agent according to following reactions respectively.

$2KMnO_4 + 3H_2SO_4 + 10NO_2 + 2H_2O \longrightarrow K_2SO_4 + 2MnSO_4 + 10HNO_3$

$SO_2 + H_2O + NO_2 \longrightarrow H_2SO_4 + NO$

* N_2O_4 is mixed anhydride of HNO_3 and HNO_2

☞ N_2O_5 : (a) $2N_2O_5 \xrightarrow{\Delta} 2N_2O_4 + O_2$

(b) $N_2O_5 + 2NaOH \longrightarrow 2NaNO_3 + H_2O$

(c) $N_2O_5 + I_2 \longrightarrow 10\ NO_2 + I_2O_5$

(3) Oxyacids of nitrogen :

(A) NITROUS ACID (HNO_2) :

PREPARATION:

(i) By acidifying an aqueous solution of a nitrite

$Ba(NO_3)_2 + H_2SO_4 \longrightarrow 2HNO_2 + BaSO_4\downarrow$

(ii) By passing an equimolar mixture of NO and NO_2 into water:

$NO + NO_2 + H_2O \longrightarrow 2HNO_2$

PROPERTIES :

(i) It is an unstable, weak acid which is known only in aqueous solution.

(ii) On trying to concentrate, the acid decomposes as given below.

$3HNO_2 \longrightarrow HNO_3 + 2NO + H_2O$

(iii) Nitrous acid and nitrites are good oxidizing agents and convert iodides to iodine, ferrous salts to ferric, stannous to stannic and sulphites to sulphates eg.

$2KI + 2HNO_2 + 2HCl \longrightarrow 2H_2O + 2NO + 2KCl + I_2$

(iv) With strong oxidizing agents like $KMnO_4$ nitrous acid and nitrites function as reducing agents and get oxidized to NO_3^- ions:

$2KMnO_4 + 5KNO_2 + 6HCl \longrightarrow 2MnCl_2 + 5KNO_3 + 3H_2O + 2KCl$

(iii) Nitrite ion is a good coordinating agent. Both nitrogen and oxygen have lone pairs capable of forming coordinate bond with metal ions. Nitrite ion can coordinate either through N or through O.(It is an ambidentate ligand) This generates linkage isomerism. Analogous organic derivatives are also known, the nitrites, RONO and the nitro compounds RNO_2 where R is any alkyl or aryl group.

(B) NITRIC ACID (HNO_3) :

PREPARATION :

(i) Laboratory method :

$NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3$

(ii) HNO_3 is now almost exclusively manufactured by the Ostwald process. In this process NH_3 is catalytically oxidized to NO over a Pt-Rh catalyst at 1200K.

$$4NH_3 + 5O_2 \longrightarrow 4NO + 6H_2O \ \Delta H = -904 \text{ kJ}$$

About 96 to 98 % of NH_3 is converted into NO. The mixture is then diluted with air. NO combines with O_2 to give NO_2 which is absorbed in water to give HNO_3 and NO, which is then recycled.

$$2NO + O_2 \longrightarrow 2NO_2 \ ; \quad 3NO_2 + H_2O \longrightarrow 2HNO_3 + NO$$

Nitric acid can be concentrated to 68 % by distillation, when a **constant boiling mixture** is formed. More concentrated acid can be made by distilling the mixture with concentrated sulphuric acid.

PROPERTIES :

(i) Pure nitric acid is colourless liquil (bp 359°C). It decomposes readily in light giving a yellow colour due to the formation of nitrogen dioxide. It is a strong acid and is almost completely dissociated into ions in solution.

(ii) Thermal stability

$$4HNO_3 \xrightarrow{\Delta} 2H_2O + 4NO_2 + O_2$$

(iii) Oxidising properties

$$2HNO_3 \text{ (conc.)} \longrightarrow H_2O + 2NO_2 + [O] \ ; \qquad 2HNO_3 \text{ (dilute)} \longrightarrow H_2O + 2NO + 3[O]$$

(a) Oxidises H_2S to sulphur

$$H_2S + 2HNO_3 \text{ (conc.)} \longrightarrow 2H_2O + 2NO_2 + S\downarrow ; \quad 3H_2S + 2HNO_3 \text{ (dilute)} \longrightarrow 4H_2O + 2NO + 3S$$

(b) Oxidises SO_2 to H_2SO_4

$$SO_2 + 2HNO_3 \text{ (conc.)} \longrightarrow H_2SO_4 + 2NO_2\uparrow ; \quad 3SO_2 + 2H_2O + 2HNO_3 \text{ (dilute)} \longrightarrow 3H_2SO_4 + 2NO$$

☞ Similarly oxidises ferrous salts to ferric salts, halogen acids to respective halogens.

(iv) Reaction with non-metals.

$$C + 4HNO_3 \longrightarrow H_2CO_3 + H_2O + 4NO_2 \ ; S + 6HNO_3 \longrightarrow H_2SO_4 + 2H_2O + 6NO_2$$

$$I_2 + 10HNO_3 \longrightarrow 2HIO_3 + 4H_2O + 10NO_2 \ ; \qquad P + 5HNO_3 \longrightarrow H_3PO_4 + H_2O + 5NO_2$$

☞ These reactions are given with conc. HNO_3 .

(v) Reaction with metals :

(A) Metals that are more electropositive than hydrogen

(a) Action on zinc or Fe :

$$Zn + 4HNO_3 \text{ (conc.)} \longrightarrow Zn(NO_3)_2 + 2H_2O + 2NO_2 \ ; \ 4Zn + 10HNO_3 \text{ (dil.)} \longrightarrow 4Zn(NO_3)_2 + 5H_2O + N_2O$$

$$4Zn + 10HNO_3 \text{ (v.dil.)} \longrightarrow 4Zn(NO_3)_2 + NH_4NO_3 + 3H_2O$$

☞ $4Mg + 10HNO_3 \text{ (v.dil.)} \longrightarrow 4Mg(NO_3)_2 + NH_4NO_3 + 3H_2O$

(b) Action on tin :

$$Sn + 4HNO_3 \text{ (conc.)} \longrightarrow H_2SnO_3 + 4NO_2 + H_2O \ ; \ 4Sn + 10HNO_3 \text{ (dil.)} \longrightarrow 4Sn(NO_3)_2 + NH_4NO_3 + 3H_2O$$

(c) Action on lead :

$$Pb + 4HNO_3 \text{ (conc.)} \longrightarrow Pb(NO_3)_2 + 2NO_2 + 2H_2O \ ; \ 3Pb + 8HNO_3 \text{ (dil.)} \longrightarrow 3Pb(NO_3)_2 + 2NO + 4H_2O$$

(B) Metals which are less electropositive than hydrogen.

(i) Action on copper

$$Cu + 4HNO_3 \text{ (conc.)} \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

$$3Cu + 8HNO_3 \text{ (v.dil)} \longrightarrow 3Cu(NO_3)_2 + NO + 4H_2O$$

(C) Metalloids : Sb and As.

$$Sb + 5\ HNO_3 \text{ (conc.)} \longrightarrow H_3SbO_4 \text{ (antimonic acid)} + 5\ NO_2 + H_2O$$

☞ Mg & Mn only metals which produce hydrogen gas with cold (1 – 2%) HNO_3.

$Mg + 2HNO_3 \rightarrow Mg(NO_3)_2 + H_2\uparrow$; $Mn + 2HNO_3 \rightarrow Mn(NO_3)_2 + H_2\uparrow$

☞ As concentrated nitric acid (80%) behaves as an oxidizing agent and metals such as Al, Fe, Cr etc are rendered passive due to the formation of a tenacious layer of insoluble oxide on the metal surface.

☞ Noble metals such as Au, Pt, Rh, and Ir are not attacked by nitric acid. However a 1:3 mixture of conc. HNO_3 and conc. HCl known as aqua regia dissolves Au and Pt as it contains free(atomic) chlorine:

$HNO_3 + 3HCl \rightarrow 2H_2O + 2Cl + NOCl$; $Au + 3Cl + HCl \rightarrow HAuCl_4$; $Pt + 4Cl + 2HCl \rightarrow H_2PtCl_6$

Brown ring test :

$$2HNO_3 + 3H_2SO_4 + 6FeSO_4 \longrightarrow 3Fe_2(SO_4)_3 + 2NO + 4H_2O$$

$$FeSO_4 + NO + 5H_2O \longrightarrow [Fe(H_2O)_5\,NO]SO_4$$

2. PHOSPHORUS :

It is a very reactive non-metal. It catches fire in air. It occurs in nature in the form of stable phosphates. (Animal bones also contain calcium phosphate (58 %)). The important minerals are:

(i) Phosphorite, $Ca_3(PO_4)_2$ (ii) Chloraptite, $Ca_3(PO_4)_2CaCl_2$

(iii) Fluoraptite, $Ca_3(PO_4)_2CaF_2$ (iv) Vivianite, $Fe_3(PO_4)_2\cdot 8H_2O$ (v) Redonda phosphate, $AlPO_4$

ALLOTROPIC FORMS OF PHOSPHORUS:

(i) White or yellow phosphorus (P_4):

PREPARATION:

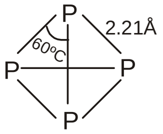
$$2Ca_3(PO_4)_2 \text{ (From bone-ash)} + 10C + 6SiO_2 \xrightarrow{\Delta} 6CaSiO_3 + 10CO + P_4(s)$$

PROPERTIES:

It is white-to-transparent and soft waxy solid. Its density is 1.8 g/cc at 20°C. Its mp and bp are 44°C and 287°C respectively. It is soluble in CS_2 but insoluble in water. It glows in dark due to slow oxidation producing yellowish-green light. This phenomenon is called phosphorescence

$$P_4 + 5O_2 \rightarrow P_4O_{10}$$

White phosphorus is poisonous. It turns yellow after some time; it is called yellow phosphorus. It undergoes oxidation in the presence of air which slowly raises its temperature and due to its low ignition temperature (~ 30°C) after a few moments it catches fire spontaneously. Due to this reason, it is strored under water.



* As readily oxidised, acts as a reducing agent.

$P_4 + 20HNO_3 \longrightarrow 4H_3PO_4 + 20NO_2 + 4H_2O$; $3CaO + 8P + 9H_2O \longrightarrow 3Ca(H_2PO_2)_2 + 2PH_3$

$$P_4 + 3CuSO_4 + 6H_2O \longrightarrow Cu_3P_2 + 2H_3PO_3 + 3H_2SO_4$$

$$Cu_3P_2 + 5CuSO_4 + 8H_2O \longrightarrow 8Cu + 5H_2SO_4 + 2H_3PO_4$$

Colloidal solution of gold may be prepared by reducing a solution of gold chloride with phosphours dissolved in ether.

(ii) Red phosphorus:

PREPARATION :

When white phosphorus is heated in the atmosphere of CO_2 or coal gas at 573 K red phosphorus is prodouced. This red phosphorus may still contain some white phosphours which is removed by boiling the mixture with NaOH where white phosphorus is converted into PH_3 gas but red phosphorus remains inert.

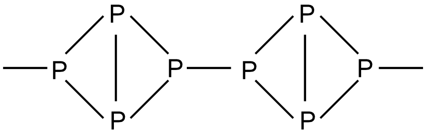
$$P_4 + 3NaOH + 3H_2O \longrightarrow PH_3(g) + 3NaH_2PO_2$$

☞ It is also prepared by heating white phosphorus with a few crystals of iodine catalyst at 250°C under high pressure in absence of air.

PROPERTIES :

It is a red crystalline solid having a density of 2.2 g/cc. It is less reactive than white phosphorus and does not dissolve in liquid CS_2. It does not catch fire at room temperature because its ignition temperature is 260°C.

It is a polymeric substance forming linear chains like this.



(iii) Black phosphorus:

It has two forms α-black phosphorus and β-black phosphorous

(a) α-black phosphorous

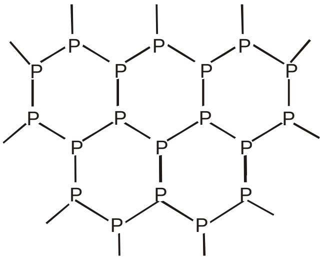
$$P(red) \xrightarrow[\text{tube 803 K}]{\text{insulated}} P(\alpha\text{-black})$$

α-black phosphorous structure is not definite and is non conductor of electricity.

(b) β-black phosphorous

$$P(white) \xrightarrow[\text{High pressure}]{\text{473 K}} P(\beta\text{-black})$$

β-black phosphorous is an electrical conductor resembling graphite in this respect and also in its flakiness and luster. It is insoluble in CS_2. It has a layered structure like graphite.



(iv) Brown phosphorus:

Above 1600°C, P_4 molecules begin to dissociate into P_2 molecules. Rapid cooling of this vapour gives brown phosphorus which probably contains P_2 molecules.

CHEMICAL PROPERTIES OF PHOSPHORUS :

☞ Reactivity of the various allotropic forms of phosphorus towards other substances decreases in the order:
Brown > white > red > black, the last one being almost inert.
Apart from their reactivity difference, all the forms are chemically similar.

(i) Action of air :

White phosphorus burns in air to form phosphorus trioxide and pentoxide.

$$P_4 + 5O_2 \longrightarrow 2P_2O_5 \;;\quad P_4 + 3O_2 \longrightarrow 2P_2O_3$$

Red and other forms of phosphorus also burn in air or oxygen but on heating.

(ii) Action of non-metals:

When heated with non-metals phosphorus forms compounds PX_3, PX_5, P_2S_3 and P_2S_5.

$$2P + 3X_2 \longrightarrow 2PX_3, \qquad 2P + 5X_2 \longrightarrow 2PX_5 \quad \text{(where X = Cl, Br, and I.)}$$

(iii) Action with metals:

Alkali metals when heated with white phosphorus in vacuum produce alkali metal phosphide, which react with water to form phosphine gas.

$$3M + P \xrightarrow{\Delta} M_3P \quad M_3P + 3H_2O \xrightarrow{\Delta} 3MOH + PH_3\uparrow \;\{\text{ where M = Na, K etc.}\}$$

(iv) Action of NaOH:

When white phosphorus is heated with NaOH solution, phosphine gas is evolved.

$$P_4 + 3NaOH + 3H_2O \longrightarrow 3NaH_2PO_2 + PH_3\uparrow$$

(v) Action of conc. HNO_3 :

When heated with conc. HNO_3, phosphorus is oxidized to H_3PO_4.

$$P + 5NHO_3 \longrightarrow H_3PO_4 + 5NO_2\uparrow + H_2O$$

(vi) **Action of conc. H_2SO_4:**

When heated with conc. H_2SO_4 phosphorus is oxidized to H_3PO_4.

$$2P + 5H_2SO_4 \xrightarrow{\Delta} 2H_3PO_4 + 5SO_2\uparrow + 2H_2O$$

☞ Conversion of white phosphorus to red phosphorus and red phosphorus to white phosphorus.

Heat in presence of I_2 catalyst at 250°C and high pressure in absence of air

White phosphorus $\rightleftharpoons$ Red phosphorus

Heat above 250°C in presence of inert gas and condense in water

COMPOUNDS OF PHOSPHORUS :

(1) PHOSPHINE :

PREPARATION:

(i) By heating white phosphorus with NaOH solution in presence of coal gas. Phosphine gas is collected by the downward displacement of water.

$$4P + 3NaOH + 3H_2O \xrightarrow{\Delta} 3NaH_2PO_2 + PH_3\uparrow$$

☞ Coal gas is used to prevent oxidation of phosphine. The phsophine gas is contaminated with a combustible gas P_2H_4. It is separated from PH_3 by passing the gaseous mixture through a freezing mixture whereupon P_2H_4 condenses to a liquid and PH_3 is collected by the downward displacement of air. Pure PH_3 does not burn in air.

(ii) By the action of alkalies on phosphonium salts:

$$PH_4I + NaOH \xrightarrow{\Delta} NaI + PH_3\uparrow + H_2O$$

(iii) By the action of dil. HCl or dil. H_2SO_4 on metal phosphides.

$$Na_3P + 3HCl \longrightarrow 3NaCl + PH_3\uparrow \;; \qquad AlP + 3HCl \longrightarrow AlCl_3 + PH_3\uparrow$$

$$2Na_3P + 3H_2SO_4 \longrightarrow 3Na_2SO_4 + 2PH_3\uparrow$$

(iv) $H_3PO_2 + 4H \xrightarrow{Zn/HCl} PH_3 + 2H_2O$

PROPERTIES :

(i) It is a colourless gas with a smell of rotten fish and is neutral to litmus paper, It is heavier than air and only slightly soluble in water, It is a poisonous gas and acts as a Lewis base.

(ii) **Action of chlorine:**

It reacts with Cl_2 to form PCl_5.

$$PH_3 + 4Cl_2 \longrightarrow PCl_5 + 3HCl$$

☞ Similar reaction occurs between heated phosphine and Br_2 and I_2 vapours.

(iii) Reaction with hydrogen halides: When PH_3 is bubbled in solution of HX, phosphonium halides are formed.

$$PH_3 + HX \longrightarrow PH_4X$$

(iv) **Action on $CuSO_4$ solution:**

When PH_3 is bubbled in acidic solution of copper sulphate, a black precipitate of copper phosphide is formed.

$$3CuSO_4 + 2PH_3 \longrightarrow Cu_3P_2\downarrow \text{\{black\}} + 3H_2SO_4$$

(v) **Reaction with $AgNO_3$ solution:**

When PH_3 gas is bubbled in a solution of $AgNO_3$, a yellow precipitate of silver phosphide, Ag_3P, is first formed which later decomposes to black Ag.

$$3AgNO_3 + PH_3 \longrightarrow Ag_3P\downarrow \text{(yellow)} + 3HNO_3$$

$$Ag_3P + 3AgNO_3 + 3H_2O \longrightarrow 6Ag\downarrow \text{(black)} + 3HNO_3 + H_3PO_3$$

(vi) **Reaction with mercuric chloride solution:**

When mercuric chloride solution is treated with PH_3 gas, a brownish black precipitate of mercuric phosphide is formed.

$$3HgCl_2 + 2PH_3 \longrightarrow Hg_3P_2\downarrow \text{ (brownish-black)} + 6HCl$$

* Samples of PH_3 can be dried using quick lime, or NaOH sticks. It cannot be dried by conc. H_2SO_4 because of its reaction with it.

USES :

It is used in making smoke signals and producing smoke screens in battle-fields.

2. OXIDES OF PHOSPHORUS :

(A) PHOSPHORUS TRIOXIDE (P_2O_3) :

PREPARATION :

It is prepared by burning phosphorus in a limited supply of oxygen when gaseous P_4O_{10} and P_4O_6 are formed. On lowering the temperature using a condenser, P_4O_6 remains in gaseous form whereas P_4O_{10} condenses as a solid which is stopped by glasswool. On passing the remaining gaseous mixture through freezing mixture, it converts into colourless crystals of P_4O_6.

PROPERTIES :

(i) It is colourless crystalline solid having mp 23.8°C and bp 178°C.

(ii) It dissolves in cold water to form phosphorus acid. It is thus the anhydride of phosphorus acid.

$$P_2O_3 + 3H_2O \rightarrow 2H_3PO_3$$

(iii) It dissolves in hot water liberating PH_3

$$2P_2O_3 + 6H_2O \longrightarrow 3H_3PO_4 + PH_3$$

(iv) It slowly gets oxidized in air to form P_2O_5

$$P_2O_3 + O_2 \longrightarrow P_2O_5$$

(v) It burns in Cl_2 gas forming phosphorus oxytrichloride ($POCl_3$) and phosphoryl chloride (PO_2Cl)

$$P_2O_3 + 2Cl_2 \longrightarrow POCl_3 + PO_2Cl$$

(B) PHOSPHORUS PENTOXIDE (P_2O_5) :

PREPARATION :

It is obtained by burning phosphorus in air.

$$P_4 + 5O_2 \longrightarrow P_4O_{10}$$

PROPERTIES:

(i) It is a white powder acidic in nature and is the anhydride of orthophosphoric acid. Its empirical formula is P_2O_5 and its molecular formula is P_4O_{10}.

(ii) It sublimes on heating at 250°C.

(iii) **Action of water:**

It dissolves in water with hissing sound forming metaphosphoric acid and finally orthophosphoric acid.

$$P_4O_{10} + 2H_2O \longrightarrow 4HPO_3 \;; \qquad HPO_3 + H_2O \longrightarrow H_3PO_4$$

(iv) **Dehydrating power:**

It dehydrates conc. H_2SO_4 and conc. HNO_3 to SO_3 and N_2O_5 respectively.

$$2HNO_3 + P_2O_5 \xrightarrow{\text{distillation}} 2HPO_3 + N_2O_5 \;;\; H_2SO_4 + P_2O_5 \xrightarrow{\text{distillation}} 2HPO_3 + SO_3$$

USES :

(i) For drying acidic gases	(ii) As a dehydrating agent
(iii) For the preparation of SO_3 and N_2O_5	(iv) For the preparation of phosphoric acid

3. OXY-ACIDS OF PHOSPHORUS :

(A) PHOSPHORUS ACID (H_3PO_3) :

PREPARATION:

(i) By dissolving P_2O_3 in water:

$$P_2O_3 + 3H_2O \longrightarrow 2H_3PO_3$$

(ii) By hydrolysis of PCl_3 with water:

$$PCl_3 + 3H_2O \qquad H_3PO_3 + 3HCl$$

The solution containing H_3PO_3 and HCl is heated to 180°C and HCl gas is driven out. The resulting solution on crystallization gives white crystals of H_3PO_3.

(iii) By heating hypophosphorus acid :

$$3H_3PO_2 \text{ (concentrated solution)} \xrightarrow{40°\text{or more}} PH_3 + 2H_3PO_3$$

PROPERTIES:

(i) It is a white crystalline solid, soluble in water and having melting point of 74°C.

(ii) It is a weak acid and a reducing agent

(iii) When neutralized with bases or alkalies, it forms neutral salts called phosphites which are unstable.

$$H_3PO_3 + 3NaOH \longrightarrow Na_3PO_3 + 3H_2O$$

Its basicity is 2 because it has only two replaceable H atoms. The third H atom is not replaceable because it is not connected to oxygen.

(iv) $4H_3PO_3 \xrightarrow{\Delta} 3H_3PO_4 + PH_3$ (Disproportionation)

(v) $H_3PO_3 + 3PCl_5 \longrightarrow PCl_3 + 3POCl_3 + 3HCl$

(vi) It is a strong reducing agent :

$$2AgNO_3 + H_3PO_3 + H_2O \longrightarrow 2Ag + 2HNO_3 + H_3PO_4$$

$$2HgCl_2 + H_3PO_3 + H_2O \longrightarrow Hg_2Cl_2 + 2HCl + H_3PO_4$$

(B) ORTHOPHOSPHORIC ACID (H_3PO_4) :

PREPARATION:

(i) By heating calcium phosphate with conc. H_2SO_4

$$Ca_3(PO_4)_2 + 3H_2SO_4 \longrightarrow 2CaSO_4 + 2H_3PO_4$$

$CaSO_4$ is insoluble. Solution of H_3PO_4 is separated from $CaSO_4$. It is then concentrated by evaporating it at 180°C and dehydrated by conc. H_2SO_4 placed in a vacuum dessicator cooled by freezing mixture. White crystals of H_3PO_4 are thus formed.

(ii) By hydrolysis of PCl_5:

$$PCl_5 + 4H_2O \longrightarrow H_3PO_4 + 5HCl$$

(iii) By heating white phosphorus with conc. HNO_3:

$$P + 5HNO_3 \longrightarrow H_3PO_4 + 5NO_2 + H_2O$$

PROPERTIES :

(i) Pure orthophosphoric acid is a white crystalline solid highly soluble in water having melting point of 42°C. It is a weak acid. It forms two acid salts and one normal salt.NaH_2PO_4 is sodium dihydrogen phosphate,Na_2HPO_4 is disodium hydrogen phosphate & Na_3PO_4 is sodium orthophosphate.

(ii) **Action of heat :**

$$H_3PO_4 \xrightarrow{220°C} H_4P_2O_7 \text{ (pyrophosphoric acid) ;} \qquad H_4P_2O_7 \xrightarrow{316°C} HPO_3 \text{ (metaphosphoric acid)}$$

(iii) **Neutralization with alkalies or bases:**

$$H_3PO_4 \xrightarrow[-H_2O]{NaOH} NaH_2PO_4 \text{ (pri. phosphate)} \xrightarrow[-H_2O]{NaOH} NaHPO_4 \text{ (sec. phosphate)} \xrightarrow[-H_2O]{NaOH} Na_3PO_4 \text{ (tert. phosphate)}$$

☞ $NaH_2PO_4 \xrightarrow{\Delta} NaPO_3 + H_2O$

USES:

It is used as a laboratory reagent and in manufacture of medicines.

GROUP SIXTEEN ELEMENTS : THE OXYGEN FAMILY

Oxygen, sulphur, selenium, tellurium and polonium constitute group 16 of the periodic table. This is sometimes known as group of chalcogens. The name is derived from the greek word for brass and points to the association of sulphur and its congeners with copper. Most copper minerals contain either oxygen or sulphur and frequently the other members of the group.

Occurrence :

Oxygen is the most abundant of all the elements on the earth. Oxygen forms about 46.6% by mass of earth's crust . Dry air contains 20.946% oxygen by volume.

However, the abundance of sulphur in the earth's crust is only 0.03-0.1%. Combined sulphur exists primarily as sulphates such as gypsum $CaSO_4.2H_2O$, epsom salt $MgSO_4 .7H_2O$, baryta $BaSO_4$ and sulphides such as galena PbS, zinc blende ZnS, copper pyrites $CuFeS_2$. Traces of sulphur occur as hydrogen sulphide in volcanoes.

Selenium and tellurium are also found as metal selenides and tellurides in sulphide ores. Polonium occurs in nature as a decay product of thorium and uranium minerals.

Electronic Configuration :

The elements of group 16 have six electrons in the outermost shell and have $ns^2 np^4$ general electronic configuration.

Atomic and Ionic Radii :

Due to increase in the number of shells , atomic and ionic radii increase from top to bottom in the group. The size of oxygen atoms is however, exceptionally small .

Ionisation Enthalpy :

Ionisation enthalpy decrease down the group. It is due to increase in size. However, the element of this group have lower ionisation enthalpy values compared to those of group 15 in the corresponding periods. This is due to the fact that group 15 element have extra stable half-filled p orbitals elelctronic configurations.

Electron Gain Enthalpy :

Because of the 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.

Electronegativity :

Next to fluorine, oxygen has the highest electronegativity value amongst the elements. Within the group, electronegativity decrease with an increase in atomic number. This implies that the metallic character increase from oxygen to polonium.

Physical Properties :

Oxygen and sulphur are non-metal, selenium and tellurium metalloids, whereas polonium is a metal. Polonium is radioactive and is short lived (Half-life 13.8 days). All these element exhibit allotropy. The melting and boiling points increase with an increase in atomic number down the group. The larger difference between the melting and boiling points of oxygen and sulphur may be explained on the basis of their atomicity; oxygen exist as diatomic molecules (O_2) whereas sulphur exists as polyatomic molecule (S_8).

ATOMIC & PHYSICAL PROPERTIES :

Element		O	S	Se	Te
Atomic Number		8	16	34	52
Atomic Mass		16	32.06	78.96	127.6
Electronic configuration		[He] $2s^2$ $2p^4$	[Ne] $3s^2$ $3p^4$	[Ar] $3d^{10}4s^2$ $4p^4$	[Kr] $4d^{10}5s^2$ $5p^4$
Covalent Radius / pm		74	103	119	142
Ionic Radius X^{-2} / pm		140	184	198	221
Ionization enthalpy / (kJ mol^{-1})	I	1314	1000	941	869
	II	3388	2251	2045	1790
Electronegativity		3.5	2.44	2.48	2.01
Density/[g cm^{-3} (293 K)]		1.32	2.06	4.19	6.25
Melting point / K		54	393	490	725
Boiling point / K		90	718	958	1260

Chemical Properties :

Oxidation states and trends in chemical reactivity :

The elements of group 16 exhibit a number of oxidation states. The stability of -2 oxidation state decreases down the group. Polonium hardly shows -2 oxidation states. Since electronegativity of oxygen is very high, it shows only negative oxidation states as -2 except in the case of OF_2 where its oxidation states is + 2. Other elements of the group exhibit + 2 + 4 + 6 oxidation states but + 4 and + 6 are more common. Sulphur, selenium and tellurium usually show + 4 oxidation in their compounds with oxygen and +6 oxidations state with fluorine. The stability of +6 oxidation state decreases down the group and stability of + 4 oxidation state increases (inert pair effect). Bonding in + 4 and + 6 oxidation states are primarily covalent.

Anomalous behaviour of oxygen :

The anomalous behaviour of oxygen, like other member of p-block present in second period is due to its small size and high electronegativity. One typical example of effects of small size and high electronegativity is the presence of strong hydrogen bonding in H_2O which is not found in H_2S.

The absence of d orbitals in oxygen limits its covalency to four and in practice, rarely exceeds two. On the other hand, in case of other elements of the group, the valence shell can be expanded and covalence exceeds four.

(i) **Reactivity with hydrogen :** All the elements of group 16 form hydrides of the type H_2E (E = S, Se., Te, Po). Some properties of hydrides are given in Table. Their acidic character increases from H_2O to H_2Te. The increase in acidic character can be explained in terms of decrease in bond (H-E) dissociation enthalpy down the group. Owing to the decrease in bond (H-E) dissociation enthalpy down the group, the thermal stability of hydrides also decreases from H_2O to H_2Po. All the hydrides except water possess reducing property and this character increases from H_2S to H_2Te.

Table : Properties of Hydrides of Group 16 Elements

Property	H_2O	H_2S	H_2Se	H_2Te
m.p./K	273	188	208	222
b.p./K	373	213	232	269
H-E distance/pm	96	134	146	169
HEH angle (º)	104	92	91	90
$\Delta_f H$/kJ mol^{-1}	-286	-20	73	100
Δ_{diss} H (H-E)/kJ mol^{-1}	463	347	276	238
Dissociation constant[a]	1.8×10^{-16}	1.3×10^{-7}	1.3×10^{-4}	2.3×10^{-3}

(ii) **Reactivity with oxygen :** All these elements form oxides of the EO_2 and EO_3 types where E = S, Se, Te or Po. Ozone (O_3) and sulphur dioxide (SO_2) are gases while selenium dioxide (SeO_2) is solid. Reducing property of dioxide decreases from SO_2 to TeO_2 ; SO_2 is reducing while TeO_2 is an oxidising agent. Besides EO_2 type sulphur, selenium and tellurium also form EO_3 type oxide (SO_3, SeO_3, TeO_3). Both types of oxides are acidic in nature.

(iii) **Reactivity toward the halogens :** Elements of group 16 form a larger number of halides of the type EX_6, EX_4 and EX_2 where E is an element of the group and X is an halogen. The stabilities of the halides decrease in the order F > Cl > Br > l. Amongst hexahalides, hexafluorides are the only stable halides. All hexafluorides are gaseous in nature. They have octahedral structure. Shulphur hexafluoride $SF_{\backslash 6}$ is exceptionally stable for steric reasons.

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

All elements except selenium form dichlorides and dibromides. These dihalides are formed by sp^3 hybridisation and thus have tetrahedral structure. The well known 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 :

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

1. DIOXYGEN (O_2) :

It differs from the remaining elements of the VIth group because of the following properties.

(A) small size (B) high electronegativity and (C) non-availability of d-orbitals.

PREPARATION :

(i) By thermal decomposition of oxides of metals.

$$2\ HgO \xrightarrow{450^0C} 2\ Hg + O_2 ; \qquad 2\ Ag_2O \xrightarrow{350^0C} 4\ Ag + O_2$$

$$3\ MnO_2 \xrightarrow{\Delta} Mn_3O_4 + O_2 ; \qquad 2\ Pb_3O_4 \xrightarrow{\Delta} 6\ PbO + O_2$$

(ii) By thermal decomposition of oxygen rich compounds.

$$2\ NaNO_3 \xrightarrow{\Delta} 2NaNO_2 + O_2 \ ; \quad 2\ KClO_3 \xrightarrow{\Delta} 2\ KCl + 3O_2 \text{ (laboratory method)}$$

$$4\ K_2Cr_2O_7 \xrightarrow{\Delta} 4\ K_2CrO_4 + 2\ Cr_2O_3 + 3O_2 \ ; 2\ KMnO_4 \xrightarrow{\Delta} K_2MnO_4 + MnO_2 + O_2$$

(iii) By the action of conc. H_2SO_4 on MnO_2.

$$2\ MnO_2 + 2H_2SO_4 \longrightarrow 2\ MnSO_4 + 2H_2O + O_2$$

(iv) By the action of water on Na_2O_2.

$$2\ Na_2O_2 + 2\ H_2O \longrightarrow 4\ NaOH + O_2$$

(v) By the action of conc. H_2SO_4 on $KMnO_4$ or $K_2Cr_2O_7$.

$$4\ KMnO_4 + 6\ H_2SO_4 \longrightarrow 2\ K_2SO_4 + 4MnSO_4 + 6H_2O + 5O_2$$

$$2\ K_2Cr_2O_7 + 8H_2SO_4 \longrightarrow 2\ K_2SO_4 + 2Cr_2(SO_4)_3 + 8H_2O + 3O_2$$

(vi) **By Brins process (mfg.) :**

$$2\ BaO + O_2(air) \xrightarrow{500^0C} 2BaO_2 \ ; 2\ BaO_2 \xrightarrow{800^0C} 2\ BaO + O_2$$

(vii) **From air (mfg.) :**

Oxygen is obtained by liquification of air and then its fractional distillation.

PROPERTIES:

Colourless , odourless and tasteless gas. It is paramagnetic and exhibits allotropy. Three isotopes of oxygen are $^{16}_{8}O$, $^{17}_{8}O$ and $^{18}_{8}O$. Oxygen does not burn but is a strong supporter of combustion.

USE :

(i) Oxygen mixed with helium or CO_2 is used for artificial respiration. **(ii)** Liquid oxygen is used as oxidising agent in rocket fuels. **(iii)** Oxygen is used for production of oxy-hydrogen or oxy-acetylene flames employed for cutting and welding.

2. OXIDES :

(i) Acidic oxides

They dissolve in water forming oxyacids , e.g., CO_2, SO_2 , SO_3, N_2O_5 , N_2O_3 , P_4O_6 , P_4O_{10}, Cl_2O_7, CrO_3 , Mn_2O_7 , V_2O_5.

$$Cl_2O_7 + H_2O \longrightarrow 2\,HClO_4\,;\ Mn_2O_7 + H_2O \longrightarrow 2\,HMnO_4$$

(ii) Basic oxides

They either dissolve in water to form alkalies or combine with acids to form salts and water or combine with acidic oxides to form salts; e.g., Na_2O, CaO. CuO, FeO, BaO etc.

$$Na_2O + H_2O \longrightarrow 2\,NaOH\,;\ CaO + H_2O \longrightarrow Ca(OH)_2\,;\ CuO + H_2SO_4 \longrightarrow CuSO_4 + H_2O$$

(iii) Neutral Oxides

They neither combine with acids nor with the bases to form salts e.g., CO, N_2O, NO etc.

(iv) Amphoteric Oxides

These can combine with acids as well as bases e.g., ZnO, Al_2O_3, BeO, Sb_2O_3, Cr_2O_3, PbO etc.

$$PbO + 2\,NaOH \longrightarrow Na_2\,PbO_2 + H_2O\,;\quad PbO + H_2SO_4 \longrightarrow PbSO_4 + H_2O$$

$$Cr_2O_3 + 2\,NaOH \longrightarrow Na_2Cr_2O_4 + H_2O;\ Cr_2O_3 + 3\,H_2SO_4 \longrightarrow Cr_2(SO_4)_3 + 3\,H_2O$$

(v) Mixed Oxides

They behave as mixture of two simple oxides,

e.g., Pb_3O_4 ($2PbO + PbO_2$), Fe_3O_4 ($FeO + Fe_2O_3$), Mn_3O_4 ($2\,MnO + MnO_2$)

(vi) Peroxides

They react with dilute acids and form H_2O_2, e.g., Na_2O_2, K_2O_2, BaO_2 etc.

$$Na_2O_2 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O_2$$

They react with water forming O_2 .

$$Na_2O_2 + H_2O \longrightarrow 2NaOH + 1/2O_2$$

(vii) Dioxides

Like peroxide, they contain excess of oxygen but do not yield H_2O_2 with dil. acids e.g. PbO_2, MnO_2 etc. They evolve Cl_2 with conc. HCl and O_2 with conc. H_2SO_4.

$$MnO_2 + 4HCl \longrightarrow MnCl_2 + Cl_2 + 2H_2O;\ 2MnO_2 + 2H_2SO_4 \longrightarrow 2MnSO_4 + O_2 + 2H_2O$$

(viii) Super Oxides

They contain O_2^- ion, e.g., KO_2 , RbO_2 and CsO_2 . These oxides react with water forming H_2O_2 and O_2

$$2\,KO_2 + 2\,H_2O \longrightarrow 2\,KOH + H_2O_2 + O_2.$$

(ix) Sub Oxides

They contain less oxygen than expected from the normal valency of the elements e.g., C_3O_2, N_2O, Pb_2O, Hg_2O etc.

☞ $C_3O_2 \longrightarrow O=\underset{sp}{C}=\underset{sp}{C}=\underset{sp}{C}=O$

2. OZONE (O_3) :

PREPARATION:

It is prepared by passing silent electric discharge through pure and dry oxygen

$$O_2 \xrightarrow{\text{energy}} O + O$$

$$O_2 + O \longrightarrow O_3\,;\ \Delta H = 2845\ kJ\ mol^{-1}$$

$$3O_2 \rightleftharpoons 2O_3$$

☞ Mixture obtained contains 5-10% ozone by volume and this mixture is called ozonised oxygen. The apparatus used for this is called as ozoniser ((i) Simen’s and (ii) Brodie’s ozonisers).

PROPERTIES :

(i) Pale blue gas which forms a blue liquid on cooling and on solidification forms violet black crystals. It has a strong fish-like smell and is slightly soluble in water but more in turpentine oil, glacial acetic acid or CCl_4. O_3 molecule is diamagnetic but O_3^- is paramagnetic.

(i) **Oxidising agent :**

$$O_3 + 2H^+ + 2\bar{e} \longrightarrow O_2 + H_2O \text{ ; SRP = + 2.07 v (In acidic medium)}$$

$$O_3 + H_2O + 2\bar{e} \longrightarrow O_2 + 2OH^- \text{ ; SRP = + 1.24 v (In alkaline medium)}$$

Therefore, ozone is a strong oxidising agent in acidic medium.

(a) It oxidises I^- to I_2 (from neutral solution of KI)

$$O_3 \longrightarrow O_2 + [O]$$
$$2\,KI + H_2O + [O] \longrightarrow 2\,KOH + I_2$$
$$\overline{2\,KI + H_2O + [O] \longrightarrow 2\,KOH + O_2 + I_2}$$

☞ Alkaline KI is oxidised to potassium iodate & periodate.

$KI + 3O_3$ $\quad$ $KIO_3 + 3O_2$; $\quad$ $KI + 4O_3$ $\quad$ $KIO_4 + 4O_2$

Similarly S^{2-} $\quad$ SO_4^{2-} (but not H_2S), NO_2^- $\quad$ NO_3^-, SO_3^- $\quad$ SO_4^{2-}, AsO_3^{3-} $\quad$ AsO_4^{3-} , MnO_4^{2-} $\quad$ MnO_4^- , Sn^{2+} $\rightarrow$ Sn^{+4} & $[Fe(CN)_6]^{4-} \rightarrow [Fe(CN)_6]^{3-}$ in acidic medium.

(b) It oxidises moist S, P, As into their oxy acids.

$$O_3 \longrightarrow O_2 + [O] \times 3$$
$$S + 3\,[O] \longrightarrow SO_3$$
$$SO_3 + H_2O \longrightarrow H_2SO_4$$
$$\overline{S + 3O_3 + H_2O \longrightarrow H_2SO_4 + 3O_2}$$

(c) It oxidises H_2S to S

$$H_2S + O_3 \longrightarrow H_2O + S \downarrow \text{(yellow)}$$

(ii) **Reaction with dry I_2:**

$$2\,I_2 + 9[O_3] \longrightarrow I_4O_9 + 9O_2$$

☞ I_4O_9 yellow solid has the composition $I^{+3}\,(IO_3^-)_3$. Formation of this compound is a direct evidence in favour of basic nature of I_2 (i.e. its tendency to form cations).

(iii) **Reaction with moist iodine :**

$$O_3 \longrightarrow O_2 + [O] \times 5$$
$$I_2 + 5[O] \longrightarrow I_2O_5$$
$$I_2O_5 + H_2O \longrightarrow 2HIO_3$$
$$\overline{5O_3 + I_2 + H_2O \longrightarrow 2HIO_3 + 5O_2}$$

(iv) **Reaction with Silver :**

Silver articles become black in contact with ozone.

$$Ag + O_3 \longrightarrow Ag_2O \downarrow \text{(black)} + O_2$$

(v) **Reaction with H_2O_2 :**

$$2e^- + 2H^+ + O_3 \longrightarrow O_2 + H_2O$$
$$H_2O_2 \longrightarrow O_2 + 2H^+ + 2e^-$$
$$\overline{\underset{\text{Oxidising agent}}{O_3} + \underset{\text{Reducing agent}}{H_2O_2} \longrightarrow 2O_2 + H_2O}$$

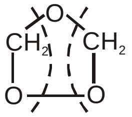
It is supported by the fact that SRP of ozone is higher (+2.07) than SRP of hydrogen peroxide (+1.77). Therefore , ozone is stronger oxidising agent than hydrogen peroxide.

(vi) **Bleaching Action :**

O_3 also bleaches coloured substances through oxidation

(vii) **Ozonolysis :**

Alkenes, alkynes react with ozone forming ozonides.

$CH_2 = CH_2 + O_3 \longrightarrow$  $\xrightarrow[-ZnO]{Zn+H_2O}$ 2HCHO

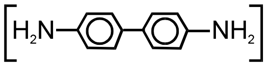
(viii) **Reaction with KOH :**

Forms orange coloured compound, potassium ozonide.

$$2\,KOH + 5O_3 \longrightarrow 2\overset{+}{K}O_3^{-} + 5O_2 + H_2O$$

(orange solid)

TESTS FOR OZONE

(i) A filter paper soaked in a alcoholic benzidine  becomes brown when brought in contact with O_3 (this is not shown by H_2O_2)

(ii) **Tailing of mercury**

Pure mercury is a mobile liquid but when brought in contact with O_3 its mobility decreases and it starts sticking to glass surface forming a type of tail due to the dissolution of Hg_2O (mercury sub-oxide) in Hg.

$2\,Hg + O_3 \longrightarrow Hg_2O + O_2$

USES :

(i) As a germicide and disinfectant for sterilising water and improving the atmosphere of crowded places.

(ii) For detecting the position of double bond in the unsaturated organic compounds.

(iii) In mfg. of artificial silk, synthetic camphor, $KMnO_4$ etc.

3. HYDROGEN PEROXIDE (H_2O_2) :

PREPARATION :

(i) Laboratory method

$BaO_2 . 8H_2O + H_2SO_4$ (cold) $\longrightarrow BaSO_4 \downarrow$ (white) $+ H_2O_2 + 8H_2O$

$BaSO_4$ is filtered to get aqueous hydrogen peroxide.

☞ $Ba(OH)_2 + H_2O_2 + 6H_2O \longrightarrow BaO_2 . 8H_2O$

☞ $BaO_2 + 2HCl$ (ice cold) $\longrightarrow BaCl_2 + H_2O_2$

Not possible to isolate H_2O_2 from this solution as $BaCl_2$ is soluble in water

☞ The reaction between anhydrous BaO_2 and H_2SO_4 is slow and practically ceases after sometimes due to the formation of a protective layer of $BaSO_4$ on BaO_2.

☞ Since H_2SO_4 can decompose H_2O_2 at a higher temperature, therefore, the reaction should be carried out at low temperature or H_3PO_4 can be used in place of H_2SO_4

$3BaO_2 + 2H_3PO_4 \longrightarrow Ba_3((PO_4)_2 \downarrow + 3H_2O_2$; $Ba_3(PO_4)_2 + 3H_2SO_4 \longrightarrow 3BaSO_4 \downarrow + 2H_3PO_4$

H_3PO_4 can be used again.

(ii) By electrolysis of conc. H_2SO_4 at 0^0C using inert electrodes (platinum).

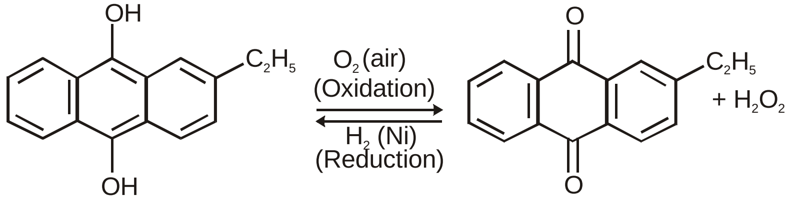
$$H_2SO_4 \rightleftharpoons H^{\oplus} + HSO_4^{\ominus}$$

at anode : → $2HSO_4^{\ominus} \longrightarrow S_2O_8^{2-} + 2H^+ + 2\bar{e}$; at cathode : → $H^+ + \bar{e} \longrightarrow \frac{1}{2}H_2$

$H_2S_2O_8 + H_2O \xrightarrow[\text{distillation}]{80-90^0C} 2H_2SO_4 \xrightarrow{BaCl_2} BaSO_4 \downarrow$ (white) + H_2O_2 (aq)

$BaSO_4$ is removed by filteration to get aqueous H_2O_2.

(iii) **Industrial method (Auto oxidation):**



2- Ethyl anthraquinol 2-Ehtylanthraquinone

$K_2S_2O_8$ (s) + $2D_2O \longrightarrow 2KDSO_4$(aq) + $D_2O_2(\ell)$

PROPERTIES :

(i) Colourless viscous liquid which appears blue in the larger quantity and is soluble in water (due to H- bonding) in all proportions and form a hydrate $H_2O_2.H_2O$ (mp 221 K)

(ii) Its boiling point 144^0C more than water but freezing point (-4) less than water. Density and dielectric constant are also higher than H_2O

(iii) Its aqueous solution is more stable than the anhydrous liquid where it decomposes into water and O_2 slowly on exposure to light.

$2H_2O_2 \longrightarrow 2H_2O + O_2$

H_2O_2 is not kept in glass containers because traces of alkali metal ions from the glass can catalyse the explosive decomposition of H_2O_2 Therefore, aqueous solution is stored in plastic or wax-lined glass containers and some urea or phosphoric acid or glycerol is added to that solution because these compounds have been found to behave as negative catalyst for the decomposition of H_2O_2

(iv) **Acidic nature :**

Behaves as a weak acid according to the following equation

$H_2O_2 \text{ (aq)} \rightleftharpoons H^+ + HO_2^-$; $K_a = 1.5 \times 10^{-12}$ at 25^0 C

Aqueous solution of H_2O_2 turns blue litmus red which is then bleached by the oxidising property of H_2O_2

$Na_2CO_3 + H_2O_2 \longrightarrow Na_2O_2 + H_2O + CO_2$

$Ba(OH)_2 + H_2O_2 + 6H_2O \longrightarrow BaO_2 . 8H_2O \downarrow$

☞ A 30% H_2O_2 solution has pH = 4.0

(v) **Oxidising Agent :**

$2\bar{e} + 2H^+ + H_2O_2 \longrightarrow 2H_2O$; SRP = + 1.77 v (In acidic medium)

$2\bar{e} + H_2O_2 \longrightarrow 2OH^-$; SRP = + 0.87 v (In alkaline medium)

☞ On the basis of the above potentials, we can say that H_2O_2 is strong oxidising agent in acidic medium but kinetically it is found that reactions are faster in basic medium.

(A) **In acidic medium :**

(a) It oxidises PbS to $PbSO_4$.

$H_2O_2 \longrightarrow H_2O + [O] \times 4$

$PbS + 4[O] \longrightarrow PbSO_4$

$PbS + 4H_2O_2 \longrightarrow PbSO_4 + 4H_2O$

This property is utilised in restoring the white colours in old paintings which turns black due to the formation of PbS by the action of atmospheric H_2S.

(b) H_2O_2 oxidises H_2S to sulphur.

$H_2O_2 \longrightarrow H_2O + [O]$

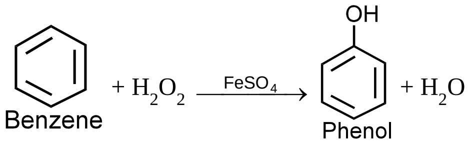
$H_2S + [O] \longrightarrow H_2O + S\downarrow$

$H_2O_2 + H_2S \longrightarrow 2H_2O + S\downarrow$

☞ H_2O_2 in acidic medium also oxidises $AsO_3^{3-} \rightarrow AsO_4^{3-}$, $SO_3^{2-} \rightarrow SO_4^{2-}$, $KI \rightarrow I_2$, $S^{2-} \rightarrow SO_4^{2-}$, $FeSO_4 \rightarrow Fe_2(SO_4)_3$ & $[Fe(CN)_6]^{4-} \rightarrow [Fe(CN)_6]^{3-}$

(c) $NH_2 - NH_2$ (hydrazine) $+ 2H_2O_2 \longrightarrow N_2 + 4H_2O$

(d)



(B) In alkaline medium :

(a) $Cr(OH)_3\,(s) + 4\,NaOH + 3H_2O_2 \longrightarrow 2Na_2CrO_4\,(aq.) + 8H_2O$

or

$10\,OH^- + 3\,H_2O_2 + 2\,Cr^{3+} \longrightarrow 2\,CrO_4^{2-} + 8H_2O$

(b) $2NaBO_2 + 2H_2O_2 + 6H_2O \longrightarrow Na_2\,[(OH)_2\,B(O\text{-}O)_2\,B(OH)_2]\,6H_2O$ (sodium per oxoborate)

☞ Used as a brightner in washing powder.

(vi) Reducing Agent :

It acts as a reducing agent towards powerful oxidising agnet.

$H_2O_2 \longrightarrow O_2 + 2H^+ + 2\bar{e}$

☞ In alkaline solution, its reducing character is more than in acidic medium.

$2\,OH^- + H_2O_2 \longrightarrow O_2 + 2H_2O + 2\bar{e}$

(a) Ag_2O is reduced to Ag.

$Ag_2O + H_2O_2 \longrightarrow 2Ag + H_2O + O_2$

(b) It reduces O_3 to O_2.

$H_2O_2 + O_3 \longrightarrow H_2O + 2O_2$

(c) It reduces ferric cyanide to ferrous cyanide (basic medium).

$2\,K_3\,[Fe(CN)_6] + 2KOH \longrightarrow K_4[Fe(CN)_6] + H_2O + O$

$H_2O_2 + O \longrightarrow H_2O + O_2$

$2K_3[Fe(CN)_6] + 2KOH + H_2O_2 \longrightarrow 2K_4\,[Fe(CN)_6] + 2H_2O + O_2$

☞ It also reduces $MnO_4^- \rightarrow Mn^{2+}$ (acidic medium), $MnO_4^- \rightarrow MnO_2$ (basic medium), $OCl^- \rightarrow Cl^-$, $IO_4^- \rightarrow IO_3^-$ & $Cl_2 \rightarrow Cl^-$

TESTS FOR H_2O_2 :

(i) With $K_2Cr_2O_7$

$K_2Cr_2O_7 + H_2SO_4 + H_2O_2 \longrightarrow K_2SO_4 + 2\,CrO_5 + 5\,H_2O$

or

$Cr_2O_7^{2-} + 2H^+ + 4H_2O_2 \longrightarrow 2CrO_5 + 5H_2O$

☞ CrO_5 bright blue coloured compound soluble in ether.

$CrO_5 + H_2SO_4 \longrightarrow 2Cr_2\,(SO_4)_3 + 6H_2O + 7O_2$

(ii) $2\,HCHO + H_2O_2 \xrightarrow[\text{pyrogallol}]{OH^-} 2\,HCOOH + H_2$

When this reaction is carried out in dark, it is accompanied by emission of light (yellow coloured). It is an example of chemiluminescene.

(iii) An acidified solution of titanium salt gives yellow or orange colour with H_2O_2.

$Ti^{+4} + H_2O_2 + 2H_2O \longrightarrow H_2TiO_4$ (yellow/orange) $+ 4H^+$

USES :

(i) In bleaching of delicate materials such as silk, wool, cotton, ivory etc.

(ii) As a valuable antiseptic and germicide for washing wounds, teeth and ears under the name perhydrol.

(iii) As 'antichlor' to remove traces of chlorine and hypochlorite.

(iv) As oxidising agent in rocket fuels

4. SULPHUR (S) :

Sulphur Allotropic Froms :

Sulphur forms numerous allotropes of which the **yellow rhombic** (α - sulphur) and **monoclinic** (β - sulphur) forms are the most important. The stable forms at room temperature is rhombic sulphur, which transfroms to monoclinic sulphur when heated above 369 K.

Rhombic sulphur (~:- sulphur) :

This allotrope is yellow in colour , m.p. 385.8 K and specific gravity 2.06. Rhombic sulphur crystals are formed on evaporating the solution of roll sulphur in CS_2. It is insoluble in water but dissolved to some extent in benzene, alcohol and ether. It is readily soluble in CS_2 .

Monoclinic sulphur (- sulphur) :

Its m.p. is 393 K and specific gravity 1.98. It is soluble in CS_2. This form of sulphur is prepared by melting rhombic sulphur in a dish and cooling till crust is formed. Two holes are made in the crust and the remaining liquid poured out. On removing the crust, colourless needle shaped crystals of β - sulphur are formed. It is stable above 369 K and transforms into α - sulphur below it . Conversely, α - sulphur is stable below 369 K and transfroms into β - sulphur above this. At 369 K both the forms are stable. This temperature is called transition temperature.

Both rhombic and monoclinic sulphur have S_8 molecules these S_8 molecules are packed to give different crystal structures. The S_8 ring in both the forms is puckered and has a crown shape. The molecular dimensions are given in figure.

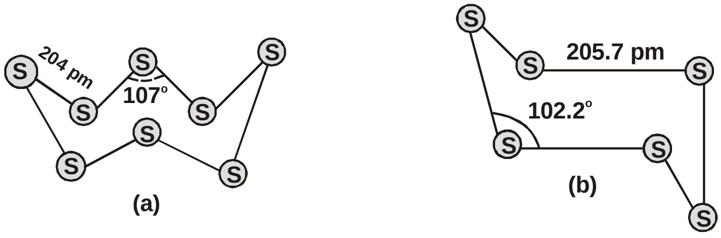


Fig. : The structures of (a) S_8 ring in rhombic sulphur and (b) S_6 form

Several other modifications of sulphur containing 6-20 sulphur atoms per ring have been synthesised in the last two decades. In cyclo- S_6, the ring adopts the chair form and the moleculatr dimension are as shown in fig. (b) At elevated temperatures (~ 1000 K), S_2 is the dominant species and is paramagnetic like O_2.

3. COMPOUNDS OF SULPHUR :

(A) SODIUM THIOSULPHATE ($Na_2S_2O_3$ .5H_2O) :

PREPARATION :

(i) $Na_2SO_3 + S \xrightarrow[\text{in absence of air}]{\text{boiled}} Na_2S_2O_3$

(ii) $Na_2CO_3 + 2SO_2$ (excess) $+ H_2O \longrightarrow 2NaHSO_3 + CO_2$; $2NaHSO_3 + Na_2CO_3 \longrightarrow 2Na_2S_2O_3 + H_2O + CO_2$

(iii) $2\ NaHS + 4NaHSO_3 \longrightarrow 3Na_2S_2O_3 + 3H_2O$

(iv) $Na_2S + Na_2SO_3 + I_2 \longrightarrow Na_2S_2O_3 + 2\,NaI$

(V) $2Na_2S_3 + 3O_2$ (from air) $\xrightarrow{\Delta} 2Na_2S_2O_3 + 2S$

PROPERTIES :

(i) It is a colourless crystalline substance soluble in water which loses water of crystallisation on strong heating

(ii) **As antichlor :**

It removes the chlorine from the surface of fibres (while dyeing) according to following reaction.

$Na_2S_2O_3 + Cl_2 + H_2O \longrightarrow Na_2SO_4 + 2HCl + S$

Therefore , it is known as antichlor

(iii) **Reaction with HCl :**

$Na_2S_2O_3 + HCl \longrightarrow 2NaCl + SO_2 + S + H_2O$

This test is used for distinction between $S_2O_3^{2-}$ and SO_3^{2-} ions as SO_3^{2-} ions give only SO_2 with HCl.

(iv) **Complex formation reactions :**

(a) **Reaction with silver salts ($AgNO_3$, AgCl, AgBr or AgI) :**

$Na_2S_2O_3 + 2AgNO_3 \longrightarrow Ag_2S_2O_3 \downarrow$ (white) $+ 2\,NaNO_3$

$Ag_2S_2O_3 + H_2O \longrightarrow Ag_2S \downarrow$ (Black) $+ H_2SO_4$

If hypo is in excess, then soluble complex is formed.

$2Na_2S_2O_3 + AgNO_3 \longrightarrow Na_3[Ag(S_2O_3)_2]$ (soluble complex) $+ NaNO_3$

This reaction is utilized in photography where hypo is used as fixer.

(b) **Reaction with $FeCl_3$:**

It develops a pink or violet colour which soon vanishes according to following reaction.

$Fe^{3+} + 2S_2O_3^{2-} \longrightarrow [Fe(S_2O_3)_2]^-$ (Pink or violet)

$[Fe(S_2O_3)_2]^- + Fe^{3+} \longrightarrow 2Fe^{2+} + S_4O_6^{2-}$

(c) **Reaction with $AuCl_3$** (Soluble in water) :

$AuCl_3 + Na_2S_2O_3 \longrightarrow AuCl\downarrow + Na_2S_4O_6 + 2HCl$

$AuCl + Na_2S_2O_3 \longrightarrow Na_3\,[Au(S_2O_3)_2]$ (soluble complex) + NaCl

(d) **Reaction with $CuCl_2$:**

$2\,CuCl_2 + 2Na_2S_2O_3 \longrightarrow 2CuCl\downarrow + Na_2S_4O_6 + 2\,NaCl$

$CuCl + Na_2S_2O_3 \longrightarrow Cu_2S_2O_3\downarrow + 2\,NaCl$

$3\,Cu_2S_2O_3 + 2\,Na_2S_2O_3 \longrightarrow Na_4\,[Cu_6(S_2O_3)_5]$ (soluble complex)

(e) **Reaction with bismuth :**

$Bi^{3+} + 3\,Na_2S_2O_3 \longrightarrow Na_3[Bi(S_2O_3)_3]$ (soluble complex) $+ 3Na^+$

But it soon decomposes to give black ppt. of Bi_2S_3

(v) **Reaction with $HgCl_2$:**

$Na_2S_2O_3 + HgCl_2 \longrightarrow Hg_2S_2O_3 + 2NaCl$

$\downarrow + H_2O$

$HgCl_2\,.\,2HgS \xleftarrow{HgCl_2} HgS\downarrow$ (Black)

(vi) **As reducing agent In iodometric titration :**

(a) $I_2 + 2S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-}$

(b) $2\,KMnO_4 + Na_2S_2O_3 \longrightarrow K_2SO_4 + Na_2SO_4 + Mn_2O_3$

(viI) $4Na_2S_2O_3\,.5H_2O \xrightarrow[-H_2O\,(All)]{215°C} 4Na_2S_2O_3 \xrightarrow{220°C} 3Na_2SO_4 + Na_2S_5$

USES :

(i) As an ‘antichlor’ to remove excess of chlorine from bleached fabrics.

(ii) In photography as fixer.

(iii) As a reagent in idometric and idiometric titrations.

(B) HYDROGEN SULPHIDE (H_2S) :

PREPARATION:

(i) $FeS + H_2SO_4 \longrightarrow FeSO_4 + H_2S$

It is prepared in kipp's apparatus

(ii) Preparation of pure H_2S gas

Sb_2S_3 (pure) + 6 HCl (pure) $\longrightarrow 2\ SbCl_3 + 3\ H_2S$

PROPERTIES :

(i) Colourless gas with rotten egg smell

(ii) Moderately soluble in water but solubility decreases with increasing temperature.

(iii) **Reducing Agent :**

Acts as a strong reducing agent as it decomposes evolving hydrogen.

(a) $H_2S + X_2 \longrightarrow 2\ HX + S;$

(b) $H_2S + SO_2 \xrightarrow{\text{moisture}} H_2O + S;$

(c) $H_2O_2 + H_2S \longrightarrow H_2O + S + O_2$

(d) $2HNO_3 \longrightarrow H_2O + 2NO_2 + [O]$

$$\begin{array}{c} H_2S + [O] \longrightarrow H_2O + S \\ \hline 2HNO_3 + H_2S \longrightarrow 2H_2O + NO_2 + S \end{array}$$

☞ It also reduces $KMnO_4 \rightarrow Mn^{2+}$, $H_2SO_4 \rightarrow SO_2$ & $K_2Cr_2O_7 \rightarrow Cr^{3+}$

(iv) **Acidic Nature :**

Its aquesous solution acts as a weak dibasic acid according to following reaction

$H_2S \rightleftharpoons HS + H^+ \rightleftharpoons S^{2-} + 2H^+$

Therefore, It forms two series of salts as given below

$NaOH + H_2S \longrightarrow NaHS + H_2O$; $NaOH + H_2S \longrightarrow Na_2S + 2H_2O$

(v) **Formation of Polysulphides :**

They are obtained by passing H_2S gas through metal hydroxides.

$Ca(OH)_2 + H_2S \longrightarrow CaS + 2H_2O$; $CaS + 4\ H_2S \longrightarrow CaS_5 + 4H_2$

$NH_4OH + H_2S \longrightarrow (NH_4)_2S + 2H_2O$; $(NH_4)_2S + H_2S$ (excess) $\longrightarrow (NH_4)_2\ S_{x+1} + xH_2$

yellow ammonium sulphide

TESTS FOR H_2S :

(i) Turns acidified lead acetate paper black

(ii) Gives violet or purple colouration with sodium nitropruside solution.

USES :

(i) As a loboratory reagent for the detection of basic radicals in qualitative analysis.

(ii) As reducing agnet.

(C) SULPHUR DIOXIDE :

PREPARATION :

(i) $S + O_2$ or air $\xrightarrow{\text{Burn}} SO_2$

(ii) $S + 2H_2SO_4$ (conc.) $\xrightarrow{\Delta} 3SO_2 + 2H_2O$

(iii) By heating Cu or Ag with conc. H_2SO_4

$Cu + H_2SO_4 \longrightarrow CuSO_4 + 2H_2O + SO_2$

(iv) By reaction of metal sulphites with dil.HCl

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

Similarly bisulphites also give SO_2 with dil. HCl

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

(v) By heating sulphides in excess of air

$2\,ZnS + 3O_2 \longrightarrow 2ZnO + 2SO_2$

(vi) $CaSO_4$ (gypsum) + C $\xrightarrow[1000^{0}C]{\Delta}$ 2 CaO + SO_2 + CO_2

☞ By this method SO_2 is obtained in large scale

PROPERTIES :

(i) Colourless gas with burning sulphur smell.

(ii) It is heavier than air and is highly soluble in water\

(iii) Neither burns nor helps in burning but burning magnesium and potassium continue to burn in its atmosphere.

$3Mg + SO_2 \longrightarrow 2\,MgO + MgS$; $4K + 3SO_2 \longrightarrow K_2SO_3 + K_2S_2O_3$

(iv) **Acidic Nature :**

Acidic oxide and thus dissolve in water forming sulphurous acid.

$SO_2 + H_2O \longrightarrow H_2SO_3$

(v) **Addition Reaction :**

$SO_2 + Cl_2 \xrightarrow{\text{Sun light}} SO_2Cl_2$ (sulphuryl chloride)

$SO_2 + O_2 \underset{\text{Asbests}}{\overset{\text{platinised}}{\rightleftharpoons}} SO_3$; $PbO_2 + SO_2 \longrightarrow PbSO_4$

(vi) **Reducing Nature :**

$H_2O + SO_2 \longrightarrow H_2SO_3$; $H_2SO_3 + H_2O \longrightarrow H_2SO_4 + 2H$

☞ Reducing character is due to the liberation of nascent hydrogen

(a) Reduces halogens to corresponding halides

$$\begin{array}{l} SO_2 + 2H_2O \longrightarrow H_2SO_4 + 2H \\ 2H + Cl_2 \longrightarrow 2HCl \\ \hline SO_2 + 2H_2O + Cl_2 \longrightarrow H_2SO_4 + 2HCl \end{array}$$

(b) Reduces acidified iodates to iodine

$$\begin{array}{l} SO_2 + 2H_2O \longrightarrow H_2SO_4 + 2H] \times 5 \\ 2KIO_3 + H_2SO_4 \longrightarrow K_2SO_4 + 2HIO_3 \\ 2HIO_3 + 10H \longrightarrow I_2 + 6H_2O \\ \hline 2KIO_3 + 5SO_2 + 4H_2O \longrightarrow K_2SO_4 + 4H_2SO_4 + I_2 \end{array}$$

☞ It also reduces acidified $KMnO_4 \longrightarrow Mn^{2+}$ (decolourises),

Acidified $K_2Cr_2O_7 \longrightarrow Cr^{3+}$ (green coloured solution) & Ferric Sulphate $\longrightarrow$ Ferrous sulphate

(vii) **Oxidising nature :**

Acts as oxidising agent with strong reducing agent

(a) $2H_2S + SO_2 \xrightarrow{\text{moisture}} 2H_2O + 3S$

(b) $2SnCl_2 + SO_2 + 4HCl \longrightarrow 2SnCl_4 + 2H_2O + S$

(c) $2Hg_2Cl_2 + SO_2 + 4HCl \longrightarrow 2HgCl_2 + 2H_2O + S$

(d) $2CO + SO_2 \longrightarrow 2CO_2 + S$

(e) $2\,Fe + SO_2 \longrightarrow 2FeO + FeS$

(viii) **Bleaching Action :**

$SO_2 + 2H_2O \longrightarrow H_2SO_4 + 2H$

This is due to the reducing nature of SO_2

Coloured matter + H $\underset{\text{Air oxidation}}{\rightleftharpoons}$ colourless matter.

Therefore, bleaching is temporary

USES :

(i) Used in manufacture of H_2SO_4 & paper from wood pulp.
(ii) As a bleaching agent for delicate articles like wool, silk and straw.
(iii) Used in refining of petroleum and sugar.

(D) SULPHUR TRIOXIDE (SO_3) :

PREPARATION:

(i) $6H_2SO_4 + P_4O_{10} \longrightarrow 6SO_3 + 4H_3PO_4$

☞ P_4O_{10} is dehydrating agent

(ii) $Fe_2(SO_4)_3 \xrightarrow{\Delta} Fe_2O_3 + 3SO_3$

(iii) $2SO_2 + O_2 \overset{pt}{\rightleftharpoons} 2SO_3$

PROPERTIES:

(i) **Acidic Nature :**

Dissolves in water forming sulphuric acid

$SO_3 + H_2O \longrightarrow H_2SO_4$

(ii) $H_2SO_4 + SO_3 \longrightarrow H_2S_2O_7$ (oleum)

(iii) $SO_3 + HCl \longrightarrow SO_2(OH)Cl$ (chlorosulphuric acid)

(iv) **Oxidising Nature :**

(a) $2SO_3 + S \xrightarrow{100^0C} 3SO_2$

(b) $5SO_3 + 2P \longrightarrow 5SO_2 + P_2O_5$

(c) $SO_3 + PCl_5 \longrightarrow POCl_3 + SO_2 + Cl_2$

(d) $SO_3 + 2HBr \longrightarrow H_2O + Br_2 + SO_2$

USES:

(i) Used in manufacture of H_2SO_4 and oleum.
(ii) Used as a drying agent for gases.

(E) SULPHURIC ACID (H_2SO_4) :

PREPARATION:

(i) $2FeSO_4 . 7H_2O \xrightarrow{dist.} Fe_2O_3 + H_2SO_4 + SO_2 + 13H_2O$

(ii) **Lead Chamber Process (Industrial method) :**

$2SO_2 + O_2$ (air) $+ 2H_2O +$ [NO] (catalyst) $\longrightarrow 2H_2SO_4 +$ [NO] (catalyst)

Acid obtained is 80% pure and is known as brown oil of vitriol

(iii) **Contact process (Industrial method) :**

$O_2 + 2SO_2 \overset{catalyst}{\rightleftharpoons} 2SO_3$

The commonly used catalysts are platinum, ferric oxide or vanadium pentoxide. V_2O_5 is preferred as it is cheaper and is not poisoned by impurities

H_2SO_4 (58%) $+ SO_3 \longrightarrow H_2S_2O_7$ (oleum)

Sulphuric acid of any desired concentration can be obtained from oleum by dilution with water.

$H_2S_2O_7 + H_2O \longrightarrow 2H_2SO_4$

Oxidation of sulphur dioxide is reversible and exothermic. According to Le-chatelier principle, the favourable conditions for the greater yield of sulphur trioxide are.

(a) An excess of air- SO_2 and oxygen are taken in 2:3 molecular proportion

(b) Low tempt-optimum tempt. 450^0C

(c) Higher pressure-one atmosphere

PROPERTIES :

(i) A colourless syrupy liquid (it is H-bonded)

(ii) It fumes strongly in moist air and is highly corrosive in nature.

(iii) **Thermal decomposition :**

$H_2SO_4 \overset{440^\circ C}{\rightleftharpoons} H_2O + SO_3$

(iv) **Acidic Nature :**

It is a strong dibasic acid and ionises as

$H_2SO_4 \rightleftharpoons H^+ + HSO_4^- \rightleftharpoons 2H^+ + SO_4^{2-}$

(a) Forms two series of salts

$NaOH + H_2SO_4 \longrightarrow NaHSO_4$ (sodium bisulphate) + H_2O

$NaHSO_4 + NaOH \longrightarrow Na_2SO_4$ (sodium sulphate) + H_2O

(b) Decomposes carbonates and bicarbonates into carbon dioxide

$Na_2CO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O + CO_2$

$NaHCO_3 + H_2SO_4 \longrightarrow NaHSO_4 + H_2O + CO_2$

(c) Displaces more volatile acids from their metal salts.

$2NaCl + H_2SO_4 \longrightarrow Na_2SO_4 + HCl$

$2NaNO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + 2HNO_3$

$CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 2HF$

(v) **Oxidising Nature :**

H_2SO_4 acts as a strong oxidising agent

$2H_2SO_4 + 2e^- \longrightarrow SO_4^{2-} + 2H_2O + SO_2$

or

$H_2SO_4 \longrightarrow H_2O + SO_2 + [O]$

(a) Non-metals (carbon, sulphur etc) are oxidised to their oxides.

$H_2SO_4 \longrightarrow H_2O + SO_2 + O] \times 2$

$C + 2[O] \longrightarrow CO_2$

$C + 2H_2SO_4 \longrightarrow CO_2 + 2SO_2 + 2H_2O$

$2P + 5H_2SO_4 \longrightarrow 2H_3PO_4 + 5SO_2 + 2H_2O$

(b) Metals (copper, silver, mercury etc.) are oxidised to their oxides which then combine with acid to form corresponding sulphates.

$H_2SO_4 \longrightarrow H_2O + SO_2 + [O]$

$Cu + [O] \longrightarrow CuO$

$CuO + H_2SO_4 \longrightarrow CuSO_4 + H_2O$

$Cu + 2H_2SO_4 \longrightarrow CuSO_4 + SO_2 + 2H_2O$

(c) Iodine is liberated from KI

$2\,KI + H_2SO_4 \longrightarrow K_2SO_4 + 2HI$

$H_2SO_4 \longrightarrow H_2O + SO_2 + [O]$

$2\,HI + [O] \longrightarrow I_2 + H_2O$

$2\,KI + 2H_2SO_4 \longrightarrow K_2SO_4 + SO_2 + I_2 + 2H_2O$

Here HI is oxidised to I_2. Similarly bromine is liberated from KBr

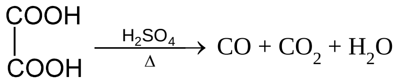
(d) $C_{10}H_8$ (naphthalene) + $9H_2SO_4 \xrightarrow[\text{catalyst}]{\text{Hg as}} C_8H_6O_4$ (phthalic acid) + $10H_2O + 9SO_2 + 2CO_2$

(vi) **Dehydrating agent :**

Sulphuric acid acts as a powerful dehydrating agent because it has a great affinity for water

(a) $C_{12}H_{22}O_{11}$ (cane sugar) $\xrightarrow[-11\,H_2O]{H_2SO_4}$ 12C

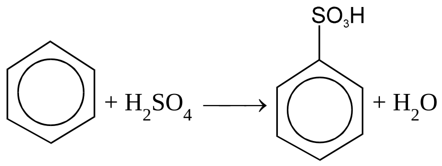
(b)



$$\begin{array}{c}COOH\\ |\\ COOH\end{array} \xrightarrow[\Delta]{H_2SO_4} CO + CO_2 + H_2O$$

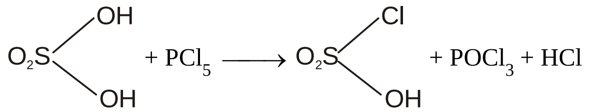
(vii) **Miscellaneous reactions :**

(a) Sulphonation of aromatic compounds

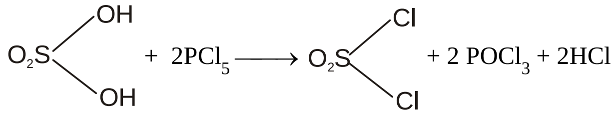


Benzene Benzene sulphonic acid

(b) **Reaction with PCl_5 :**



Chlorosulphonic acid



Sulphury chloride

(c) $K_4[Fe(CN)_6] + 6H_2SO_4 + 6H_2O \longrightarrow 2K_2SO_4 + FeSO_4 + 3(NH_4)_2SO_4 + 6CO$

(d) $3KClO_3 + 3H_2SO_4 \xrightarrow{\Delta} 3\,KHSO_4 + HClO_4 + 2ClO_2 + H_2O$

(e) $H_2SO_4 + P_2O_5 \longrightarrow 2HPO_3 + SO_3$

USES :

(i) For the manufacture of fertilizer such as ammonium sulphate and super phosphate of lime.
(ii) As an important laboratory reagent.
(iii) In storage batteries.
(iv) In leather, textile, paper and dyeing industries.

GROUP 17 ELEMENTS : THE HALOGEN FAMILY

Fluorine, chlorine, bromine, iodine and astatine are members of Group 17. These are collectively known as the halogens (Greek halo means salt and genes born i.e., salt producers). The halogens are highly reactive non-metallic elements.

Electronic Configuration :

All these elements have seven electrons in their outermost shell ($ns^2\,np^5$) which is one electron short of the next noble gas.

Atomic and Ionic Radii :

The halogens have the smallest atomic radii in their respective periods due to maximum effective nuclear charge . Atomic and ionic radii increase from fluorine to iodine due to increasing number of quantum shells.

Ionisation Enthalpy :

They have little tendency to lose electron. Thus they have very high ionisation enthalpy. Due to increase in atomic size, ionisation enthalpy dereases down the group.

Electron Gain Enthalpy :

Halogen have maximum negative electrons gain enthalpy in the corresponding period. This is due to the fact that the atoms of these elements have only one electron less than stable noble gas configurations. Electron gain enthalpy of the elements of the group becomes less negative down the group. However, the negative electron gain enthalpy of fluorine is less than that of chlorine. It is due to small size of fluorine atom. As a result, there are strong interelectronic repulsions in the relatively small 2p orbitals of fluorine and thus, the incoming electron does not experience much attraction.

Electronegativity :

They have very high electronegativity. The electronegativity decreases down the group. Fluorine is the most electronegative element in the periodic table

Physical Properties :

Fluorine and chlorine are gases, bromine is a liquid and iodine is a solid. Their melting and boiling points steadily increase with atomic number. All halogen are coloured. This is due to absorption of radiations in visible region which results in the excitation of outer electrons to higher energy level. By absorbing different quanta of radiation, they display different colours. For example, F_2, has yellow, Cl_2, greenish yellow, Br_2, red and I_2, violet colour. Fluorine and chlorine react with water. Bromine and iodine are only sparingly soluble in water. But are soluble in organic solvents such as chloroform, carbon tetrachloride, carbon disulphide and hydrocarbons to give coloured solutions.Except the smaller enthalpy of dissociation of F_2 compared to that of Cl_2 whereas X-X bond dissocitation enthalpies from chlorine onwards show the expected trend: Cl – Cl > Br – Br > I – I . A reason for this anomaly is the relatively larger electrons- electron repulsion among the lone pairs in F_2 molecule where they are much closer to each other than in case of Cl_2.

ATOMIC & PHYSICAL PROPERTIES :

Element	F	Cl	Br	I
Atomic Number	9	17	35	53
Atomic Mass	19	35.45	79.90	126.90
Electronic configuration	[He] $2s^2\ 2p^5$	[Ne] $3s^2\ 3p^5$	[Ar] $3d^{10}4s^2\ 4p^5$	[Kr] $4d^{10}5s^2\ 5p^5$
Covalent Radius / pm	64	99	114	133
Ionic Radius X^- / pm	133	184	196	220
Ionization enthalpy / (kJ mol^{-1})	1680	1256	1142	1008
Electron gain enthalpy /(kJ mol^{-1})	– 333	– 349	– 325	– 296
Distance X -X/pm	143	199	229	266
Enthalpy of dissociation (X_2)/kJ mol^{-1}	158.8	242.6	192.8	151.1
Electronegativity	4	3.2	3.0	2.7
Melting point / K	54.4	172	265.8	386.6
Boiling point / K	84.9	239.0	332.5	458.2

Chemical Properties

Oxidation states and trends in chemical reactivity

All the halogens exhibit –1 oxidation state. However, chlorine, bromine and iodine exhibit + 1, + 3, + 5 and + 7 oxidation states also. The higher oxidation states of chlorine, bromine and iodine are realised mainly when the halogens are in combination with the small and highly electronegative fluorine and oxygen atoms e.g., in interhalogens, oxides and oxoacids.

The fluorine atom has no d orbitals in its valence shell and therefore cannot expand its octet. Being the most electronegative, it exhibits only – 1 oxidation state.

All the halogens are highly reactive. They react with metals and non-metals to form halides. The reactivity of the halogens decreases down the group.

The ready acceptance of an electron is the reason for the strong oxidising nature of halogens. F_2 is the strongest oxidising halogen and it oxidises other halide ions in solution or even in the solid phase. The decreasing oxidising ability of the halogen in aqueous solution down the group is evident from their standard electrode potentials. Fluorine oxidises water to oxygen whereas chlorine and bromine react with water to form corresponding hydrohalic and hypohalous acids. The reactions of iodine with water is non- spontaneous . I^- can be oxidised by oxygen in acidic medium; just the reverse of the reaction observed with fluorine.

$$2F_2(g) + 2H_2O(\ell) \rightarrow 4H^+(aq) + 4F^-(aq) + O_2(g)$$

$$X_2(g) + H_2O(\ell) \rightarrow HX(aq) + HOX(aq)$$

(where X = Cl or Br)

$$4I^-(aq) + 4H^+(aq) + O_2(g) \rightarrow 2I_2(s) + 2H_2O(\ell)$$

Standard Reduction Potential (SRP)

$X_2 + 2e^- \longrightarrow 2X^-$

$F_2 + 2e^- \longrightarrow 2F^-$ $\varepsilon° = +2.87$ V ; $Cl_2 + 2e^- \longrightarrow 2Cl^-$ $\varepsilon° = +1.36$ V

$Br_2 + 2e^- \longrightarrow 2Br^-$ $\varepsilon° = +1.09$ V ; $I_2 + 2e^- \longrightarrow 2I^-$ $\varepsilon° = +0.54$ V

☞ More the value of the SRP, more powerful is the (algebraically) oxidising agent. Hence the order of oxidising power is $F_2 > Cl_2 > Br_2 > I_2$
Since SRP is the highest for F_2 (among all elements of P.T.), it is a strogenst oxidising agent.

☞ F_2 is more powerful oxidising agent than O_3 [Inspite of 3 'O's in O_3]

Note : E.A. and I.E. values pertain to atoms in gas phase where as redox phenomena occurs in gaseous medium.
Hence properties in the gas phase cannot reflect parallely in solution phase.
Electrode potential values would be the monitoring parameter in solution phase because they are experimental (based on the correct situation).

Hydration energy of X^-

Smaller the ion, higher is the hydration energy

F^-	Cl^-	Br^-	I^-
515 kJ/mol	381	347	305

Anomalous behaviour of fluorine :

The anomalous behviour of fluorine is due to its small size, highest electronegativity, low F- F bond dissociation enthalpy, and non availability of d orbitals in valence shell. Most of the reactions of fluorine are exothermic (due to the small and strong bond formed by it with other elements). It forms only one oxoacid while other halogen form a number of oxoacids. Hydrogen fluoride is liquid (b.p. 293 K) due to strong hydrogen bonding. Other hydrogen halides are gases.

(i) Reactivity towards hydrogen:

They all react with hydrogen to give hydrogen halides but affinity for hydrogen decreases from fluorine to iodine. They dissolve in water to form hydrohalic acids. The acidic strength of these acids varies in the order : HF < HCl < HBr < HI. The stability of these halides dereases down the group due to decrease in bond (H–X) dissociation enthalpy in the order :
H – F > H – Cl > H –Br > H – I .

(ii) Reactivity towards oxygen :

Halogens form many oxides with oxygen but most of them are unstable. Fluorine forms two oxides OF_2 and O_2F_2. However, only OF_2 is the thermally stable at 298 K. These oxide are essentially oxygen fluorides because of the higher electronegativity of flurorine than oxygen . Both are strong fluorinating agents. O_2F_2 oxidises plutonium to PuF_6 and the reactions is used in removing plutonium as PuF_6 from spent nuclear fuel.

Chlorine, bromine and iodine form oxides in which the oxidation states of these halogen range from + 1 to + 7. A combination of kinetic and thermodynamic factors lead to the generally decreasing order of stability oxides formed by halogens, I > Cl > Br. The higher oxides of halogens tend to be more stable than the lower ones.

Chlorine oxides, Cl_2O, ClO_2, Cl_2O_6 and Cl_2O_7 are highly reactive oxidising agents and tend to explode. ClO_2 is used as a bleaching agent for paper pulp and textiles and in water treatment.

The bromine oxides, Br_2O, BrO_2, BrO_3 are the least stable halogen oxides and exist only at low temperature. They are very powerful oxidising agents.

The iodine oxides, I_2O_4, I_2O_5, I_2O_7 are insoluble solids and decompose on heating. I_2O_5 is very good oxidising agent and is used in the estimation of carbon monoxide.

(iii) Reactivity towards metals:

Halogen react with metals to form metal halides. For e.g., bromine reacts with magnesium to give magnesium bromide.

(iv) Reactivity of halogen towards other halogens :

Halogens combine amongst themselves to form a number of compounds known as interhalogen of the types AB, AB_3, AB_5 and AB_7 where A is a larger size halogen and and B is smaller size halogen.

1. FLUORINE (F_2) :

PREPARATION:

(i) Electrolytic method :

Electrolyte : Molten KHF_2 (1 part) + HF (5 part)
Anode : Carbon
Cathode : Steel
Vessel : Monel metal

On Electrolysis

Cathode : $2H^+ + 2e^- \longrightarrow H_2(g)$

Anode : $2F^- \longrightarrow F_2 + 2e^-$

The F_2 gas thus evolved must be free from HF which is more corrosive than fluorine.
In order to make flourine free from HF, the gas is passed through NaF which absorbs HF.

☞ Anode of carbon should be free from graphide because F_2 reacts with graphite easily to form a polymeric susbstance known as graphite fluoride.
There should be no moisture present in the vessel otherewise fluorine will react with water.

$$3H_2O + 3F_2 \longrightarrow 6HF + O_3 \;;\quad 2F_2 + 2H_2O \longrightarrow 4HF + O_2$$

☞ It is not possible to prepare fluorine by electrolysis of aq. solution of NaF or KF. It is because when aq. solution of KF is subjected to electrolysis, there will be following two oxidation in competition at anode,

$$H_2O \longrightarrow 1/2O_2 + 2H^+ + 2e^- \qquad SOP = -1.23\text{ v}$$

and

$$F^- \longrightarrow 1/2F_2 + e^- \qquad SOP = -2.87\text{v}$$

As a matter of rule that substance will be oxidise whose SOP is higher therefore water gets oxidise at anode and not F^-.

(ii) Chemical method : From $K_2\,[MnF_6]$ - potassium hexafluoromanganate (IV)

$$K_2\,[MnF_6] + 2\,SbF_5 \longrightarrow 2K\,[SbF_6] + MnF_3 + \frac{1}{2}F_2 \;;\; \left\{\begin{matrix}\text{via} \\ MnF_4 \longrightarrow MnF_3 + \frac{1}{2}F_2\end{matrix}\right\}$$

☞ In this reaction, the stronger Lewis acid SbF_5 displaces the weaker one, MnF_4 from its salt. MnF_4 is unstable and readily decomposes to give MnF_3 and fluorine.

PROPERTIES :

(i) Diatomic, Pale green-yellow gas which appears to be almost colourless. It is heavier then air. It condenses to yellow liquid at -188^0C and yellow solute at -223^0C. It has punged oddur and is highly poisonous.

(ii) Oxidising character : It is the most powerful oxidising agent.

$$F_2 + 2NaX \longrightarrow 2NaF + X_2$$
$$(X = Cl, Br, I)$$

(a) It can oxidise all other halide ions into halogen molecules

(b) It can oxidise $\overset{+5}{ClO_3^-}$ into $\overset{+7}{ClO_4^-}$ and IO_3^- to IO_4^-

$$F_2 + ClO_3^- + H_2O \longrightarrow 2F^- + ClO_4^- + 2H^+$$

(c) It can oxidise HSO_4^- into $S_2O_8^{2-}$

$$2H\overset{(+6)}{S}O_4 + F_2 \longrightarrow 2F^- + \overset{(+6)}{S_2}O_8^{2-} + 2H^+$$

☞ Some of the O^{2-} changes to O^- in the persulphate ions (having the O^-). Hence oxygen is getting oxidised.

(iii) **Reaction with NaOH solution :** With dilute alkali forms oxygen difluoride and with concentrated alkali O_2.

$$2F_2 + 2\,NaOH\,(dil) \longrightarrow OF_2\,(g) + 2\,NaF + H_2O$$

$$2F_2 + 4\,NaOH\,(conc.) \longrightarrow O_2\,(g) + 4\,NaF + 2H_2O$$

(iv) **Reaction with NH_3 : (Distinction from other halogens)**

$$2NH_3 + 3F_2 \longrightarrow N_2 + 6\,HF$$

☞ Other halogens form explosive NX_3. with conc. NH_3 (liquor ammonia)

(v) **Reaction with H_2S :**

$$H_2S + F_2 \longrightarrow SF_6 + 2\,HF$$

☞ H_2S burns

(vi) **Reaction with SiO_2 :** It attacks glass at about 100^0C.

$$SiO_2\,(s) + 2F_2\,(g) \longrightarrow SiF_4\,(g) + O_2\,(g)$$

The reaction is slow with dry F_2 .

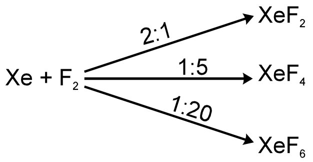
(vii) **Reaction with H_2O :**

$$2H_2O + 2F_2 \longrightarrow 4\,HF + O_2$$

sometime a little amount of O_3 also forms

$$3H_2O + 3F_2 \longrightarrow 6HF + O_3$$

(viii) **Reaction with Xe :**



(ix) **Reaction with H_2 :**

$$H_2 + F_2 \longrightarrow 2\,HF \text{ or } H_2F_2$$

☞ This reactions occurs even in dark

(x) **Reaction with SO_3 :**

$$SO_3 + F_2 \xrightarrow[AgF]{180^oC} FSO_2OOSO_2\,F$$

(xi) **Reaction with O_2 :**

$$O_2 + F_2 \xrightarrow[\text{silent electric discharge}]{\text{only in presence of}} O_2F_2$$

(xii) **Reaction with metals and non–metals :** It combines with most of the metals. Almost all non-metals except O_2 & N_2 ignite spontaneously in presence of F_2 .

$$2\,Ag + F_2 \rightarrow 2\,AgF\ ;\ 2\,Al + 3\,F_2 \rightarrow 2\,AlF_3$$

$$C + 2\,F_2 \rightarrow CF_4\ ;\ Si + 2\,F_2 \rightarrow SiF_4$$

2. CHLORINE (Cl_2) :

PREPARATION:

(i) **Common method (Cl_2 , Br_2 , f_2) :**

$$2\,NaX + 3H_2SO_4\,(conc.) + MnO_2\,(\text{oxidising agent}) \xrightarrow{\Delta} X_2 + MnSO_4 + 2NaHSO_4 + 2H_2O$$

$$4H^+ + MnO_2 + 2X^- \longrightarrow X_2 + Mn^{+2} + 2H_2O$$

(ii) Only for Cl_2 :

(a) $NaCl + HNO_3 \longrightarrow NaNO_3 + HCl \times 3$

$HNO_3 + 3HCl \longrightarrow NOCl + Cl_2 + 2H_2O$

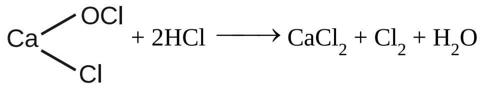
$3NaCl + 4\,HNO_3 \longrightarrow 3\,NaNO_3 + NOCl$ (nitrosyl chloride) $+ Cl_2 + 2H_2O$

$2NOCl + O_2 \longrightarrow 2NO_2 + Cl_2$; $NO_2 + H_2O \longrightarrow HNO_3$ (to be recycled)

(b) When Cl_2 is used for the chlorination of hydrocarbon the byproduct is HCl. The HCl is catalytically oxidised into H_2O & Cl_2 using copper powder mixed with rare earth chlorides.

$$4\,HCl + O_2 \xrightarrow[\text{Chloride}]{\text{Cu powder + rare earth}} 2H_2O + 2Cl_2$$

(c)



$$Ca(OCl)Cl + 2HCl \longrightarrow CaCl_2 + Cl_2 + H_2O$$

(d) $2KMnO_4 + 16\,HCl \rightarrow 2\,KCl + 2\,MnCl_2 + 5\,Cl_2 + 8\,H_2O$

(e) $PbO_2 + 4\,HCl \rightarrow PbCl_2, + Cl_2 + 2\,H_2O$

(iii) Manufacture of chlorine :

(a) Deacon's process : By oxidation of hydrogen chloride gas by atmoshperic oxygen in the presence of $CuCl_2$ (catalyst) at 723 K.

$$4\,HCl + O_2 \xrightarrow{CuCl_2} 2\,Cl_2 + 2\,H_2O$$

(b) Electrolytic process : Chlorine is obtained by the electrolysis of brine (concentrated NaCl solution). Chlorine is liberated at anode. It is also obtained as a by–product in many chemical industries.

$NaX\,(aq) \longrightarrow Na^+\,(aq) + X^-\,(aq)$

Anode : $2X^- \longrightarrow X_2 + 2e^-$

PROPERTIES :

(i) It is a greenish–yellow gas with pungent and suffocating odour. It is about 2–5 times heavier than air. It can be liquefied into greenish–yellow liquid which boils at 239 K. It is soluble in water.

(ii) At low temperature it forms a hydrate with water having formula $Cl_2 \,.\, 8H_2O$ which is infact a clathrate compound.

(iii) $H_2 + Cl_2 \xrightarrow[\text{(a zero order reaction)}]{} 2HCl\,(g)$, [$H_2 + Br_2 \rightarrow 2HBr$ is not a zero order reaction]

(iv) Reaction with NH_3 (common for Cl_2 & Br_2) :

(a) $8\,NH_3 + 3\,Cl_2 \longrightarrow N_2 + 6\,NH_4Cl$

(b) $NH_3 + \underset{\text{(excess)}}{3Cl_2} \longrightarrow NCl_3 + 3\,HCl$

(v) Reaction with alkali metal halides (KX) :

$2\,KBr + Cl_2 \longrightarrow 2KCl + Br_2$

$2KI + Cl_2 \longrightarrow 2\,KCl + I_2$

☞ Cl_2 can oxidise both Br^- & I^- but Br_2 can oxidise I^- only.

☞ F_2 is not used in aqueous reaction since it itself reacts with water.

(vi) Oxidising & bleaching properties : Chlorine water on standing loses its yellow colour due to the formation of HCl and HOCl. Hypochlorous acid (HOCl) so formed, gives nascent oxygen which is responsible for oxidising and bleaching properties of chlorine.

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

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

(ii) It is a powerful bleaching agent ; Bleaching action is due to oxidation.

$$Cl_2 + H_2O \rightarrow 2\,HCl + O$$

Coloured substance + O → Colourless substance

It bleaches vegetable or organic matter in the presence of moisture. Bleaching effect of chloride is permanent.

☞ But the bleching action of SO_2 is temporary because it takes place through reduction.

$$SO_2 + 2\,H_2O \longrightarrow H_2SO_4 + 2\,H$$
$$SO_3^{2-} + \text{Coloured material} \longrightarrow SO_4^{2-} + \text{Reduced coloured material (colourless)}$$

Reduced Coloured material (colourless) $\xrightarrow{O_2 \text{ of air}}$ Coloured material

(vii) Reaction with NaOH :

Common to Br_2 , I_2 & Cl_2 (but with F_2 it is different, OF_2 or O_2 is obtained)

(a) $2\,NaOH\text{ (cold \& dilute)} + Cl_2 \longrightarrow NaCl + NaClO + H_2O$

(b) $6\,NaOH\text{ (hot \& concentrated)} + 3\,Cl_2 \longrightarrow 5\,NaCl + NaClO_3 + 3\,H_2O$

(viii) Reaction with Hypo solution :

This reaction is common with Cl_2 & Br_2 but with I_2 it is different.

$$Na_2\overset{(+2)}{S_2}O_3 + H_2O + Cl_2 \longrightarrow Na_2\overset{(+2)}{S}O_4 + 2HCl + \overset{(o)}{S}\downarrow\text{(colloidal)}$$

In this reaction thiosulphate ions undergo disproportionation into SO_4^{2-} and S. Cl_2 is reduced to Cl^- .

(ix) Reaction with dry slaked lime, $Ca(OH)_2$: It gives bleaching powder.

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

(x) Reaction with metals & non–metals : Forms corresponding chlorides.

$$2\,Al + 3\,Cl_2 \rightarrow 2\,AlCl_3 \;;\; 2\,Na + Cl_2 \rightarrow 2\,NaCl$$
$$P_4 + 6\,Cl_2 \rightarrow 4\,PCl_3 \;;\; S_8 + 4\,Cl_2 \rightarrow 4\,S_2Cl_2$$

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

$$H_2 + Cl_2 \rightarrow 2\,HCl \;;\; H_2S + Cl_2 \rightarrow 2\,HCl + S \;;\; C_{10}H_{16} + 8\,Cl_2 \rightarrow 16\,HCl + 10\,C$$

Uses : Cl_2 is used

(i) for bleaching woodpulp (required for the manufacture of paper and rayon). bleaching cotton and textiles,

(ii) in the manufacture of dyes, drugs and organic compounds such as CCl_4 , $CHCl_3$, DDT, refrigerants, etc.

(iii) in the extraction of gold and platinum.

(iv) in sterilising drinking water and

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

3. BROMINE (Br_2) :

PREPARATION:

(i) Common method :

$$2\,NaBr + 3H_2SO_4\text{ (conc.)} + MnO_2 \xrightarrow{\Delta} Br_2 + MnSO_4 + 2NaHSO_4 + 2H_2O$$

(ii) From Sea-water :

NaCl is main component but NaBr is also present in some quantity in sea water. Cl_2 gas is passed through sea water when vapours of bromine are evolved.

$$2\,Br^-\text{ (aq)} + Cl_2 \longrightarrow 2Cl^-\text{ (aq.)} + Br_2$$

PROPERTIES :

(i) Reddish brown liquid, fairly soluble in water. It also forms hydrate like Cl_2

$(Br_2 . 8H_2O) \longleftarrow$ Clathrate compound

(ii) Rest reactions are same as with Cl_2

4. IODINE (I_2) :

PREPARATION:

(i) Common method :

$$2NaI + 3H_2SO_4 \text{ (conc.)} + MnO_2 \xrightarrow{\Delta} I_2 + MnSO_4 + 2NaHSO_4 + 2H_2O$$

(ii) From Caliche or Crude chile salt petre :

The main source of iodine is $NaIO_3$ (sodium iodate) which is found in nature with $NaNO_3$ (chile saltpetre). $NaIO_3$ is present in small amount. After crystallisation of $NaNO_3$, the mother liquor left contains $NaIO_3$ (soluble). To this solution $NaHSO_3$ is added where upon I_2 is precipitated.

$$2IO_3^- + 5HSO_3^- \longrightarrow 3\,HSO_4^- + 2SO_4^{2-} + I_2\,(s) + H_2O$$

(iii) From sea-weeds :

Sea-weeds are dried and burnt in shallow pits, ash left is called kelp. Ash on extraction with hot water dissolves out chlorides, carbonates, sulphates and iodides of sodium and potassium. The solution on concentration seperates out all leaving behind iodide in the solution. Solution is mixed with MnO_2 and concentrated H_2SO_4 in iron retorts. Liberated iodine is condensed in series of earthen-ware known as aludels.

$$2NaI + MnO_2 + 3H_2SO_4 \longrightarrow 2NaHSO_4 + MnSO_4 + I_2 + 2H_2O$$

(iv) $2KI + Cl_2 \longrightarrow 2KCl + I_2$ **(v)** $2KI + H_2O_2 \longrightarrow 2KOH + I_2$

(vi) $CuSO_4 + 2KI \longrightarrow K_2SO_4 + CuI_2$; $2CuI_2 \longrightarrow Cu_2I_2 + I_2$

☞ This I_2 gets dissolved into KI forming KI_3 , since I_3^- ions are yellow, therefore solution develops yellow colour.

PROPERTIES :

(i) It is a dark violet solid, undergoes sublimation, least soluble (among halogens) in water but much more soluble in KI(aq.) due to formation of KI_3

☞ KF_3 cannot be formed similarly since F does not have 'd' orbitals. So sp^3d hybridisation is not possible with F.

(ii) It is soluble in organic solvents like $CHCl_3$, CCl_4 etc. to get violet solutions.

(iii) Reaction with hypo :

iodometric titrations

$$S_2O_3^{2-} \text{ (thiosulphate ions)} + I_2 \longrightarrow \overset{+2.5}{S_4}O_6^{2-} \text{ (tetrathionate ions)} + 2I^-$$

This reaction is the basis of iodometric (direct I_2 titration) titration, which is carried out for the estimation of iodine using starch indicator.

(iv) Reaction with NH_3 :

$$NH_3\,(g) + I_2 \longrightarrow \text{No Reaction}$$

$$\underset{\text{(Ammonia liquor)}}{NH_3\,(aq)} + I_2\,(s) \xrightarrow[\text{A slurry is formed which can be dried and on hammering it explodes causing sound (crakers)}]{} \underbrace{NI_3 . NH_3}_{\text{an explosive (Nitrogentriiodide ammoniated)}} + 3HI$$

$$8NI_3 . NH_3 \longrightarrow 5N_2 + 9\,I_2 + 6NH_4I$$

(v) Reaction with $KClO_3$ or $KBrO_3$:

$$2\,KClO_3 + I_2 \xrightarrow{\Delta} 2\,KIO_3 + Cl_2\,;\ 2\,KBrO_3 + I_2 \xrightarrow{\Delta} 2KIO_3 + Br_2$$

(vi) **Reaction with ozone (dry) :**

$$2I_2\,(s) + 3O_3\,(g) \longrightarrow I_4O_9\,(s)$$

I_4O_9 is an ionic compound consisting of I^{3+} & $(IO_3^-)_3$ indicative of metallic character of I (low I.E, low E.N.)

☞ With NaOH there is common reaction as with Cl_2 and Br_2 . With H_2 there is reversible reaction.

OXIDES OF CHLORINE :

Chlorine dioxide (ClO_2) :

PREPARATION:

(i) $2\,ClO_3^-\,(aq) + SO_2\,(g) \xrightarrow{H^+} 2ClO_2(g) + SO_4^{2-}\,(aq)$

☞ Chlorates of sodium and potassium can be used

(ii) $2KClO_3 + 2\,H_2C_2O_4 \xrightarrow{90^\circ C} 2ClO_2(g) + 2CO_2 + K_2C_2O_4 + 2H_2O$

(iii) $2AgClO_3 + Cl_2 \xrightarrow{90^\circ C} 2AgCl \downarrow$ (white) $+ 2ClO_2 + O_2$

(iv) $Cl_2O_6 + N_2O_4 \rightleftharpoons ClO_2 + [NO_2^+]\,[ClO_4^-]$

PROPERTIES :

(i) Yellow gas at room temp, soluble in water and explosive substance. It also behaves as an oxidising agent. (It kill bacteria better than Cl_2)

(ii) **Reaction with ozone :** $2ClO_2 + 2O_3 \xrightarrow{H^+} Cl_2O_6$ (yellow solid) $+ 2O_2$

dichlorine hexa oxide

In the reaction O_3 is behaving as an oxidising agent.

☞ Cl_2O_6 (s) is a mixed anhydride of $HClO_3$ & $HClO_4$ because on dissolving in water it gives a mixture of these two acids.

☞ In solid state, Cl_2O_6 exists as ClO_2^+ & ClO_4^-.

(iii) **Reaction with alkaline H_2O_2 :**

In this reaction H_2O_2 acts as a reducing agent. It reduces ClO_2 into ClO_2^-

$$H_2O_2 \longrightarrow 2H^+ + O_2 + 2e^- \;;\quad e^- + ClO_2 \longrightarrow ClO_2^-\,] \times 2$$

$$H_2O_2 + 2ClO_2 \longrightarrow 2ClO_2^- + 2H^+ + O_2$$

or $\quad H_2O_2 + 2ClO_2 + 2OH^- \longrightarrow 2ClO_2^- + 2H_2O + O_2$

(iv) **Reaction with Hf** :

In this reaction HI behaves as a reducing agent where it reduces ClO_2 into Cl^- and itself is oxidised to I_2 .

$$[5e^- + 4\,H^+ + ClO_2 \longrightarrow Cl^- + 2H_2O] \times 2$$

$$[2I^- \longrightarrow I_2 + 2e^-] \times 5$$

$$2ClO_2 + 8H^+ + 10\,I^- \longrightarrow 5I_2 + 2Cl^- + 4H_2O$$

HYDRA ACIDS (HALOGEN ACIDS) :

HCl, HBr & HI :

PREPARATION:

(i) **By direct combination of elements :**

$$H_2 + Cl_2 \longrightarrow 2HCl$$

$$H_2 + Br_2 \xrightarrow{Pt} 2HBr$$

$$H_2 + I_2 \xrightarrow{Pt,\ 450^\circ C} 2HI$$

(ii) **By heating a halide with acid :**

$NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl$

$NaHSO_4 + NaCl \longrightarrow Na_2SO_4 + HCl$

For HCl we use H_2SO_4 as an acid, while for HBr and HI we use H_3PO_4.

(a) HCl cannot be dried over P_2O_5 (P_4O_{10}) or quick lime since they react with gas chemically.

$CaO + 2HCl \longrightarrow CaCl_2 + H_2O$

$P_4O_{10} + 3HCl \longrightarrow POCl_3 + 3HPO_3$

HCl is, hence dried by passing through conc. H_2SO_4 .

(b) HBr (or HI) cannot be prepared by heating bromide (iodide) with conc. H_2SO_4 because HBr and HI are strong reducing agents and reduce H_2SO_4 to SO_2 and get themselves oxidised to bromine and iodine respectively.

$KX + H_2SO_4 \longrightarrow KHSO_4 + HX$

$H_2SO_4 + 2HX \longrightarrow SO_2 + X_2 + 2H_2O$ (X = Br or I)

Hence, HBr and HI are prepared by heating bromides and iodides respectively with conc. H_3PO_4 .

$3KBr(KI) + H_3PO_4 \longrightarrow K_3PO_4 + 3HBr\ (HI)$

(iii) **By reaction of P_4 (Laboratory Method) :**

$P_4 + 6Br_2\ (6I_2) \longrightarrow 4PBr_3\ (4PI_3)$ (product in situ)

$PBr_3\ (PI_3) + 3H_2O \longrightarrow 3HBr\ (HI) + H_3PO_3$

(iv) **By passing H_2S / SO_2 into solutions of halogens :**

$H_2S + X_2 \longrightarrow 2HX + S$

$SO_2 + 2H_2O + X_2 \longrightarrow 2HX + H_2SO_4$

PROPERTIES :

(i) These are colourless, pungent smelling gases with acidic tastes.

(ii) It is heavier than air, can be liquified to colourless liquids.

(iii) These are neither combustible nor supporter of combustion.

(iv) When perfectly dry, they have no action on litmus, but in presence of moisture, they turn blue litumus red, showing acidic nature. Among HX, HI is the strongest and HF is the weakest acid.

(v) These are quite soluble in water.

HCl ionises as below.

$HCl(g) + H_2O\ (\ell) \rightarrow H_3O^+\ (aq) + Cl^-\ (aq)\quad K_a = 10^7$

It aqueous solution is called hydrochloric acid. High value of dissociation constant (K_a) indicates that it is a strong acid in water.

When three parts of concentrated HCl and one part of concentrated HNO_3 are mixed, aqua regia is formed which is used for dissolving noble metals, e.g., gold, platinum.

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

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

(v) Reaction with metals oxides, hydroxides and bicarbonates

$Zn + 2HCl \longrightarrow ZnCl_2 + H_2$; $MgO + 2HCl \longrightarrow MgCl_2 + H_2O$

$NaOH + HCl \longrightarrow NaCl + H_2O$; $CaCO_3 + 2HCl \longrightarrow CaCl_2 + H_2O + CO_2$

(vi) Reaction with salts, HCl decomposes salts of weaker acids.

$NaHCO_3 + HCl \longrightarrow NaCl + CO_2\uparrow + H_2O$; $Na_2S + 2HCl \longrightarrow 2NaCl + H_2S\uparrow$

$Na_2SO_3 + 2HCl \longrightarrow 2NaCl + SO_2\uparrow + H_2O$; $Na_2S_2O_3 + HCl \longrightarrow 2NaCl + SO_2\uparrow + H_2O + S$

$2NaNO_2 + 2HCl \longrightarrow 2NaCl + NO\uparrow + NO_2\uparrow + H_2O$

(vii) Reducing property and stability of hydracids :

HCl : It is quite stable and hence is oxidised by strong oxidising agents like MnO_2, $KMnO_4$, $K_2Cr_2O_7$, PbO_2, Pb_3O_4 .

(i) $MnO_2 + 4HCl \longrightarrow MnCl_2 + 2H_2O + Cl_2$

(ii) $2KMnO_4 + 16HCl \longrightarrow 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2$

(iii) $K_2Cr_2O_7 + 14HCl \longrightarrow 2KCl + 2CrCl_3 + 7H_2O + 3Cl_2$

(iv) $PbO_2 + 4HCl \longrightarrow PbCl_2 + 2H_2O + Cl_2$; (v) $Pb_3O_4 + 8HCl \longrightarrow 3PbCl_2 + 4H_2O + Cl_2$

Therefore, HCl is a weak reducing agent.

HBr : It is not very stable and hence more easily oxidised or acts as a strong reducing agents. In addition to above reducing properties of HCl, it also reduces H_2SO_4 to SO_2 which is not done by HCl.

$H_2SO_4 + HBr \longrightarrow SO_2 + Br_2 + 2H_2O$

Aqueous HBr on exposure to atmospheric oxygen is oxidised to bromine (yellow)

$4HBr + O_2 \longrightarrow 2\,Br_2 + 2H_2O$

Hf : It is least stable hydrogen halide. It is readily oxidised and thus acts as a powerful reducing agent. In addition to reaction shown by HCl, it shows following reactions also.

(a) $H_2SO_4 + 2HI \longrightarrow SO_2 + I_2 + H_2O$; $H_2SO_4 + 6HI \longrightarrow S + 3I_2 + 4H_2O$;
$H_2SO_4 + 8HI \longrightarrow H_2S + 4I_2 + 4H_2O$;

(b) $2HNO_3 + 2HI \longrightarrow 2NO_2 + I_2 + 2H_2O$ (c) $2HNO_2 + 2HI \longrightarrow 2NO + I_2 + 2H_2O$

(d) $HIO_3 + 5HI \longrightarrow 3I_2 + 2H_2O$ (e) $K_2S_2O_8 + 2HI \longrightarrow K_2SO_4 + I_2 + H_2SO_4$

(f) $2FeCl_3 + 2HI \longrightarrow 2FeCl_2 + I_2 + 2HCl$

☞ Aqueous solution of acid, if exposed to O_2 is oxidised to iodine.

$4HI + O_2 \longrightarrow 2I_2 + 2H_2O$

(viii) Reaction with ammonia :

$NH_3 + HX \longrightarrow NH_4X \uparrow$(white fumes) (where X = Cl, Br, I)

(ix) Action of halogens :

(a) Cl_2 is liberated from HCl by F_2 alone.

$F_2 + HCl \longrightarrow 2HF + Cl_2$

(b) Br_2 is liberated from HBr by F_2 and Cl_2 (not by I_2)

$2HBr + F_2 / Cl_2 \longrightarrow 2HF\ (2HCl) + Br_2$

(c) I_2 is liberated from HI by F_2, Cl_2 and Br_2

$2HI + F_2\ (Cl_2, Br_2) \longrightarrow 2HF\ (HCl, HBr) + I_2$

(x) Detection of cation:

HCl : $AgNO_3 + HCl \longrightarrow AgCl\downarrow$ (white) + HNO_3

$(CH_3COO)_2\,Pb + 2HCl \longrightarrow PbCl_2\downarrow$ (white) + $2CH_3COOH$

$Hg(NO_3)_2 + 2HCl \longrightarrow Hg_2\,Cl_2\downarrow$ (white) + $2HNO_3$

HBr : $AgNO_3 + HBr \longrightarrow AgBr\downarrow$ (pale yellow) + HNO_3

$(CH_3COO)_2\,Pb + 2HBr \longrightarrow PbBr_2\downarrow$ (white) + $2CH_3COOH$

Hf=: $AgNO_3 + HI \longrightarrow AgI\downarrow$ (bright yellow) + HNO_3

$(CH_3COO)_2\,Pb + 2HI \longrightarrow PbI_2\downarrow$ (yellow) + $2CH_3COOH$

$HgCl_2 + 2HI \longrightarrow HgI_2\downarrow$ (scarlet red) + 2HCl

HI reacts with $CuSO_4$ liberating iodine via the formation of cupric iodide (not by HCl or HBr).

$$2CuSO_4 + 4HI \longrightarrow 2CuI_2 + 2H_2SO_4 ; \quad 2CuI_2 \longrightarrow Cu_2I_2 + I_2$$

(xi) **Formation of aqua-regia :**

3 parts of conc. HCl and 1 part of conc. HNO_3 is known as aqua-regia. This is used for dissolving noble metals like Au (Gold) and Pt (Platinum).

$$3HCl + HNO_3 \longrightarrow NOCl + 2H_2O + 2Cl \text{ (reactive) } ; \quad Au + 3Cl \longrightarrow AuCl_3$$

USES :

(i) HCl is used in preparation of Cl_2, chlorides, aqua regia, glucose, (from corn starch), medicines, laboratory reagents, cleaning metal surfaces before soldering or electroplating. It is also used for extracting glue from bones and purifying bone black.

(ii) HBr is used as laboratory reagent for preparing bromo derivatives like sodium bromides and potassium bromide. These are used in medicines as sedatives.

(iii) HI is used as reducing agent in organic chemistry.

HYDROFLUORIC ACID [H_2F_2, HF] :

PREPARATION :

H_2 and F_2 combine with each other very violently (even in dark) to form HF. So simple reaction cannot be used for its preparation, special methods are employed for its preparation.

(i) **Laboratory Method :**

Anhydrous HF is obtained by heating dry potassium hydrogen fluoride in a copper retort connected with copper condenser.

$$KHF_2 \xrightarrow{\Delta} KF + HF$$

(ii) **Industrial Method :**

HF is prepared by heating fluorspar (CaF_2) with conc H_2SO_4.

$$CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 2HF$$

☞ Aqueous HF being corrosive to glass, is stored in wax lined bottles or vessel made of copper or monel.

In glass or silica bottles, it attacks them as follows:

$$Na_2SiO_3 + 6HF \longrightarrow Na_2SiF_6 + 3H_2O ; \quad CaSiO_3 + 6HF \longrightarrow CaSiF_6 + 3H_2O$$

$$SiO_2 + 4HF \longrightarrow SiF_4 + 2H_2O ; SiF_4 + 2HF \longrightarrow H_2SiF_6$$

This action of HF on silica (silicates) is used for etching glass. The glass surface to be etched is coated with wax, the design, is scratched on glass through wax coating this is then treated with 40% solution.

PROPERTIES:

(i) **It is colourless, corrosive liquid with pungent smell with high boiling point due to hydrogen bonding.**

(ii) Dry HF does not attack metals under ordinary conditions (except K), but in presence of water, it dissolves metals with liberation of hydrogen gas.

(iii) It is a weak dibasic acid (due to strong HF bond) and forms two series of salt.

$$NaOH + H_2F_2 \longrightarrow NaHF_2 + H_2O ; NaHF_2 + NaOH \longrightarrow 2NaF + H_2O$$

(iv) Concentrated acid reacts with oxides, hydroxides and carbonates.

$$2NaOH + H_2F_2 \longrightarrow 2NaF + 2H_2O : CaCO_3 + 2HF \longrightarrow CaF_2 + H_2O + CO_2$$

OXY-ACIDS OF CHLORINE :

HYPO-CHLOROUS ACID [HClO] :

PREPARATION:

(i) The acid is known only in solution, It is obtained by shaking precipitate of HgO with chlorine water.

$$2HgO + 2Cl_2 + H_2O \longrightarrow Hg_2OCl_2 \text{ (Oxychloride of mercury) } + 2HClO$$

(ii) Commercially, it is obtained by passing CO_2 through suspension of bleaching powder and then distilling.

$$2CaOCl_2 + H_2O + CO_2 \longrightarrow CaCl_2 + CaCO_3 + 2HClO$$

PROPERTIES:

(i) It is a weak acid. Its concentrated solution is yellow in colour while dilute solution is colourless. It is unstable and decomposes.

$$2HClO \longrightarrow 2HCl + O_2$$

(ii) It dissolves magnesium with evolution of hydrogen.

$$Mg + 3HClO \longrightarrow Mg(ClO)_2 + H_2$$

(iii) With alkalies, it forms salts called hypochlorites.

(iv) It acts as a powerful oxidising and bleaching agent. This is due to release of nascent oxygen easily.

$$HClO \longrightarrow HCl + O$$

CHLOROUS ACID [$HClO_2$] :

PREPARATION:

It is obtained in aqueous solution when barium chlorite suspension in water is treated with H_2SO_4 . The insoluble barium sulphate is filtered off.

$$Ba(ClO_2)_2 + H_2SO_4 \longrightarrow BaSO_4 + 2HClO_2$$

PROPERTIES:

(i) The freshly prepared solution is colourless but it soon decomposes to ClO_2 which makes the solution yellow.

$$5\ HClO_2 \longrightarrow 4\ ClO_2 + HCl + 2H_2O$$

(ii) The acid undergoes auto-oxidation.

$$2HClO_2 \longrightarrow HClO + HClO_3$$

(iii) The acid liberates iodine from KI.

$$4KI + HClO_2 + 2H_2O \longrightarrow 4KOH + HCl + 2I_2$$

CHLORIC ACID [$HClO_3$] :

PREPARATION:

This acid is only known in solutuion. The acid is preapred by the action of the dilute H_2SO_4 on barium chlorate.

$$Ba\ (ClO_3)_2 + H_2SO_4 \longrightarrow BaSO_4 \downarrow + 2HClO_3.$$

PROPERTIES:

Concentrated acid is colourless and pungent smelling liquid. It decomposes in light. However, it is stable in dark. It acts as a strong oxidising and bleaching agent in light. Organic substances like paper, cotton, wool, etc., catch fire in contact with the acid.

Per-Chloric Acid [$HClO_4$] :

PREPARATION:

It is the most stable oxy-acid of chlorine. Anhydrous $HClO_4$ is obtained by doing distillation of $KClO_4$ (potassium perchlorate), with 96-97.5% H_2SO_4 under low pressure at 90-160°C.

$$KClO_4 + H_2SO_4 \longrightarrow KHSO_4 + HClO_4$$

An aqueous solution of the acid is obtained by reacting barium perchlorate with calculated quantity of dilute H_2SO_4. The insoluble barium sulphate is removed by filtration.

$$Ba(ClO_4)_2 + H_2SO_4 \longrightarrow BaSO_4 \downarrow + 2HClO_4$$

PROPERTIES:

(i) Anhydrous $HClO_4$ is a colourless liquid which turns dark on keeping. It fumes in moist air.

(ii) It is one of the strongest acid and ionises as follows :

$$HClO_4 \longrightarrow H^+ + ClO_4^-$$

(iii) It dissolves most of the metals.

$$Zn + 2HClO_4 \longrightarrow Zn(ClO_4)_2 + H_2$$

(iv) It is an oxidising agent and explodes in contact with organic matter.

(v) $2HClO_4 + P_2O_5 \longrightarrow 2HPO_3 + Cl_2O_7$

BLEACHING POWDER ($CaOCl_2.H_2O$)

Bleaching powder is also called calcium chlorohypochlorite because it is considered as a mixed salt of hydrochloric acid and hypochlorous acid.

Ca(OCl)Cl

PREPARATION:

$$Ca(OH)_2 + Cl_2 \xrightarrow{40^0\,C} Ca(OCl)Cl + H_2O$$

Properties

(i) It is a pale yellow powder. It has a strong smell of chlorine. It is soluble in water but a clear solution is never formed due to the presence of impurities.

(ii) On long standing, it undergoes auto–oxidation into calcium chlorate and calcium chloride.

$$6\,CaOCl_2 \rightarrow Ca(ClO_3)_2 + 5\,CaCl_2$$

(iii) $2\,CaOCl_2 \xrightarrow{CoCl_2} 2\,CaCl_2 + O_2$

(iv) In presence of a little amount of a dilute acid, it loses oxygen.

$$2\,CaOCl_2 + H_2SO_4 \longrightarrow CaCl_2 + CaSO_4 + 2\,HClO$$

$$HClO \longrightarrow HCl + O$$

On account of the liberation of nascent oxygen, it shows oxidising and bleaching properties.

(a) Oxidising properties

$$CaOCl_2 + H_2S \longrightarrow CaCl_2 + H_2O + S$$

$$CaOCl_2 + 2\,KI + 2\,HCl \longrightarrow CaCl_2 + 2\,KCl + H_2O + I_2$$

$$3\,CaOCl_2 + 2\,NH_3 \longrightarrow 3\,CaCl_2 + 3\,H_2O + N_2$$

☞ It oxidises NO_2^- to NO_3^- , AsO_3^{3-} to AsO_4^{3-} and Fe^{2+} to Fe^{3+} (in acidic medium)

(b) Bleaching action

Coloured matter + [O] ⟶ colourless product.

(v) When bleaching powder reacts with dilute acids or CO_2 it liberates chlorine which is known as available chlorine.

$$CaOCl_2 + 2\,HCl \longrightarrow CaCl_2 + H_2O + Cl_2$$

$$CaOCl_2 + H_2SO_4 \longrightarrow CaSO_4 + H_2O + Cl_2$$

$$CaOCl_2 + CO_2 \longrightarrow CaCO_3 + Cl_2$$

☞ HNO_3 is a strong oxidising acid to be avoided, here.

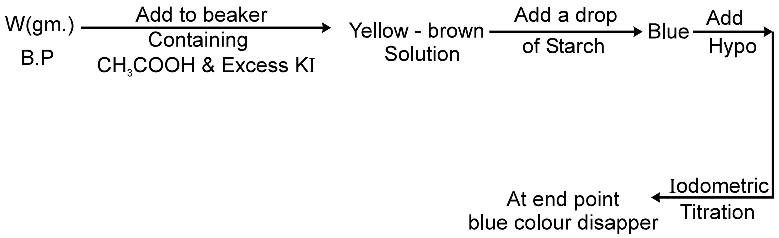
ESTIMATION OF AVAILABLE CHLORINE :

Let the wt. of sample of B.P. = W gm.

Add into a beaker containing acetic acid solution and excess KI. A yellow brown solution is formed (I_3^-)

$$I_2 + I^- \longrightarrow I_3^-$$

Now few drops of starch solution is added into it. An intensive blue color is observed. Now hypo is used as the titrant. Note the volume where the blue colour disappear.



Ĝ **Reaction involved**

$$CaOCl_2 + 2CH_3COOH \longrightarrow (CH_3COO)_2\,Ca + H_2O + Cl_2$$

$$Cl_2 + 2KI \longrightarrow 2KCl + I_2$$

$$I_2 + 2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2I^-$$

Calculation :

$$\%Cl = \frac{[M_{hypo} \times V_{hypo}] \times \frac{1}{2} \times 71}{W} \times 100$$

(vi) Bleaching powder converts acetone or ethyl alcohol into $CHCl_3$

$$CaOCl_2 + H_2O \longrightarrow Ca(OH)_2 + Cl_2$$

$$CH_3COCH_3 + 3\,Cl_2 \longrightarrow CCl_3COCH_3 + 3\,HCl$$

$$2\,CCl_3COCH_3 + Ca(OH)_2 \longrightarrow (CH_3COO)_2Ca + 2\,CHCl_3$$

Ĝ **Some important order**

(a) Acid strength :

(i) HI > HBr > HCl > HF (ii) HOCl > HOBr > HOI (iii) $HClO_4 > HClO_3 > HClO_2 > HClO$

(b) Oxidising power :

(i) $F_2 > Cl_2 > Br_2 > I_2$ (According to electrode potential)

(ii) $BrO_4^- > IO_4^- > ClO_4^-$ (iii) $HClO_4 < HClO_3 < HClO_2 \leq HClO$

(c) Order of disproportionation :

$3\,XO^- \longrightarrow 2X^- + XO_3^-$ (hypohalite ion) ; $IO^- > BrO^- > ClO^-$

PSEUDO HALOGENS & PSEUDO HALIDES:

Some inorganic compounds like $(CN)_2$ cyanogen, $(SCN)_2$ thiocyanogen, $(SeCN)_2$ selenocyanogen, $(SCSN_3)_2$ azidocarbondisulphide have been found to behave like halogens & they are known as pseudo halogen solids. Similarly few ions are known, consisting of two or more atoms of which at least one is N, that have properties similar to those of the halide ions. They are therefore called pseudohalide ions, e.g. (CN^-) cyanide ion, (SCN^-) thiocyanate ion, $(SeCN^-)$ selenocyanate ion, (OCN^-) cyanate ion, (NCN^{2-}) cyanamide ion, (N_3^-) azide ion etc.

INTERHALOGEN COMPOUNDS :

We know that halogen atoms have different electronegativity. Due to this difference in electronegativity the halogen atoms combine with each other and give rise to the formation of binary covalent compounds, which are called interhalogen compounds.These are of four types.

AB	AB_3	AB_5	AB_7
ClF	ClF_3	ClF_5	lF_7
BrF	BrF_3	BrF_5	
ICl	ICl_3	IF_5	
IF	IF_3		

PREPARATION:

(i) By the direct combination of halogens :

$Cl_2 + F_2$ (equal volumes) $\xrightarrow{473K} 2ClF$; $Cl_2 + 3F_2$ (excess) $\xrightarrow{573K} 2ClF_3$;

$I_2 + Cl_2 \longrightarrow 2ICl$;
(equimolar)

☞ Diluted with water.

$Br_2 (g) + 3F_2 \longrightarrow 2BrF_3$

☞ F_2 is diluted with N_2

$I_2 + 3F_2 \xrightarrow{-78^\circ C} 2IF_3$

☞ F_2 is taken in freon.

$Br_2 + 5F_2$ (excess) $\longrightarrow 2BrF_5$

☞ IF_7 can not be prepared by direct combination of I_2 & F_2 .

(ii) **From lower interhalogens :**

$ClF + F_2 \longrightarrow ClF_3$; $ClF_3 + F_2$ (excess) $\xrightarrow{350^\circ C} ClF_5$

$BrF_3 + F_2$ (excess) $\xrightarrow{200^\circ C} BrF_5$; $IF_5 + F_2 \xrightarrow{270^\circ C} IF_7$

☞ This method is generally applied for the preparation of halogen fluorides.

(iii) **Other methods :**

$6HCl + KIO_3 + 2KI \longrightarrow 2KCl + 3H_2O + 3ICl$

$Cl_2 + ClF_3 \xrightarrow{250-350^\circ C} 3CIF$; $KCl + 3F_2 \xrightarrow{200^\circ C} KF + ClF_5$

$3l_2 + 5AgF \longrightarrow 5Agl + lF_5$; $8F_2 + PbI_2 \longrightarrow PbF_2 + 2lF_7$

PROPERTIES:

(i) These compounds may be gases, liquids or solids.

Gases : ClF, BrF, ClF_3 , IF_7 ; Liquids : BrF_3, BrF_5 ; Solids : ICl, IBr, IF_3, ICl_3.

(ii) Interhalogens containing fluorine are colourless but inter halogens consisting of heavier halogens are coloured. The intensity of colour increases with increase in the molecular weight of the compounds.

(iii) All interhalogens are covalent molecules and are diamagnetic in nature since all the valence electrons present as bonding or non-bonding electrons are paired.

(iv) The boiling points increases with the increase in the electronegativity difference between A and B atoms.

(v) Thermal stability of AB type interhalogen compounds decreases with the decrease in electronegativity difference between A and B atoms. IF > BrF > ClF > ICl > IBr > BrCl.

☞ More polar is the A – B bond more is the stability of interhalogen.

(vi) Interhalogen compounds are more reactive than the parent halogens but less reactive than F_2.

$$ICl + 2Na \longrightarrow NaI + NaCl$$

The order of reactivity of some interhalogens is as follows :

$$ClF_3 > BrF_3 > IF_7 > BrF_5 > BrF.$$

(vii) Hydrolysis : All these undergo hydrolysis giving halide ion derived from the smaller halogen and a hypohalite (when AB), halite (when AB_3), halate (when AB_5), and perhalate (when AB_7) anion derived from the larger halogen.

$$AB + H_2O \longrightarrow HB + HOA$$

$BrCl + H_2O \longrightarrow HCl + HOBr$; $ICl + H_2O \longrightarrow HCl + HIO_2$

$ICl_3 + 2H_2O \longrightarrow 3HCl + HIO_2$; $IF_5 + 3H_2O \longrightarrow 5HF + HIO_2$

$IF_7 + 6H_2O \longrightarrow 7HF + H_5IO_6$; $BrF_5 + 3H_2O \longrightarrow 5HF + HBrO_2$

☞ Hydrolysis products are halogen acid and oxy-halogen acid. Oxy-halogen acid is of larger central halogen atom.

☞ Oxidation state of A atom does not change during hydrolysis.

(viii) Reaction with non-metallic and metallic oxides :

$4BrF_3 + 3SiO_2 \longrightarrow 3SiF_4 + 2Br_2 + 3O_2$; $4BrF_3 + 3WO_3 \longrightarrow 2WF_6 + 2Br_2 + 3O_2$

(ix) Addition reaction (of AB type compounds) :

$-CH = CH- + ICI \longrightarrow -CHI-CHCl-$; $CH_2 = CH_2 + BrCI \longrightarrow CH_2Br-CH_2Cl$

(x) Reaction with alkali metal halides :

$IBr + NaBr \longrightarrow NaIBr_2$; $ICl_3 + KCl \longrightarrow KICl_4$

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 .

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

(F)*GROUP 18 ELEMENTS : (THE ZERO GROUP FAMILY)*

Group 18 Consists of six elements: helium, neon, argon, krypton , xenon and radon . All these are gases and chemically unreactive. They form very few compounds . Because of this they are termed noble gases.

Occurrence :

All the noble gases except radon occur in the atmosphere. Their atmospheric abundabce in dry air is ~ 1% by volume of which argon is the major constituent. Helium and sometimes neon are found in minerals of radioactive origin e.g., pitch-blende, monazite, cleveite. The main commercial source of helium is natural gas. Xenon and radon are the rarest elements of the group. Radon is obtained as a decay product of ^{226}Ra.

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

☞ Most abundant element in air is Ar. Order of abundance in the air is Ar > Ne > Kr > He > Xe.

Electronic Configuration :

All noble gases have general electronic configuration ns^2np^6 except helium which has $1s^2$. Many of the properties of noble gases including their inactive nature are ascribed to their closed shell structures.

Ionisation Enthalpy :

Due to stable electronic configuration these gases exhibit very high ionisation enthalpy . However, it decreases down the group with increases in atomic size.

Atomic Radii :

Atomic radii increase down the group with increase in atomic number.

Electron Gain Enthalpy :

Since noble gases have stable electronic configurations, they have no tendency to accept the electron and therefore, have larger positive values of electron gain enthalpy.

Physical properties :

All the noble gases are monoatomic. They are colourless, and tasteless. They are sparingly soluble in water. They have very low melting and boiling points because the only type of interatomic interaction in these elements is weak dispersion forces,. Helium has the lowest boiling point (4.2K) of any known substance. It has a unusual property of diffusing through most commonly used laboratory materials such as rubber, glass or plastics.

ATOMIC & PHYSICAL PROPERTIES :

Element	He	Ne	Ar	Kr	Xe
Atomic Number	2	10	18	36	54
Atomic Mass	4	20.18	39.10	83.80	131.30
Electronic configuration	$1s^2$	$[He]\ 2s^2\ 2p^6$	$[Ne]\ 3s^2\ 3p^6$	$[Ar]\ 3d^{10}4s^2\ 4p^6$	$[Kr]\ 4d^{10}5s^2\ 5p^6$
Atomic Radius (pm)	120	160	190	200	220
Ionization enthalpy / (kJ mol^{-1})	2372	2080	1520	1351	1170
Density (at STP)/g cm^{-3}	1.8×10^{-4}	9.0×10^{-4}	1.8×10^{-3}	3.7×10^{-3}	5.9×10^{-3}
Melting point / K	–	24.6	83.8	115.9	161.3
Boiling point / K	4.2	27.1	87.2	119.7	165.0

Chemical Properties

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

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

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

The reactivity of noble gases has been investigated occasionally ever since their discovery, but all attempt to force them to react to form the compounds were unsuccessful for quite a few years. In March 1962, Neil Bartlett, then at the University of British Columbia, observed the reaction of a noble gas. First , he prepared a red compound which is formulated as $O_2^+\ PtF_6^-$. He , then realised that the first ionisation enthalpy of molecular oxygen (1175 kj mol $^{-1}$) was almost identical with that xenon (1170 kJ mol $^{-1}$). He made efforts to prepare same type of compound with $Xe^+\ PtF_6^-$ by mixing Pt F_6 and Xenon. After this discovery, a number of xenon compounds mainly with most electronegative elements like fluorine and oxygen, have been synthesised.

The compounds of krypton are fewer. Only the difluoride (KrF_2) has been studied in detali. Compounds of radon have not been isolated but only identified (e.g., RnF_2) by radiotracer technique. No true compounds of Ar, Ne or He are yet known .

☞ If Helium is compressed and liquified it forms He(I) liquid at 4.2 K. This liquid is a normal liquid like any other liquid. But if it is further cooled then He(II) is obtained at 2.2 K, which is known as super fluid, because it is a liquid with properties of gases. It climbs through the walls of the container & comes out. It has very high thermal conductivity & very low viscosity. Compounds of inert gases are of following two types.

(i) Physical compounds (possess no proper bonding)

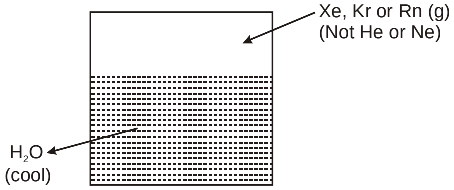
Physical compounds may be (A) compounds whose existence is on the basis of spectroscopic studies (temporary phase not isolated) and (B) clatherate compounds.

Clatherate compounds :

Inert gas molecules get trapped in the cages formed by the crystal structure of water.

During the formation of ice Xe atoms will be trapped in the cavities (or cages) formed by the water molecules in the crystal structure of ice. Compounds thus obtained are called clatherate compounds.

There are no chemical bonds. They do not possess an exact chemical formula but approx it is 6 water molecules : 1 inert gas molecule. The cavity size is just smaller than the atom of the noble gas. Such compounds are also formed by the other organic liquids like dihydroxybenzene (for example quinol).



(ii) True chemical compounds (posses proper bonding).

COMPOUNDS OF XENON :

(a) XENON DIFLUORIDE (XeF_2):

PREPARATION:

(i) $Xe + F_2 \xrightarrow[\text{Ni–Tube or monel metal (alloy of Ni)}]{873K, 1bar} XeF_2$

☞ Volume ratio should be 2:1 otherwise other higher fluorides tend to form.

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

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

(iv) Recently discovered method :

$K^+ [AgF_4]^-$ [potassium tetrafluoroargentate (III)] is first prepared and this is reacted with BF_3 .

$K^+ [AgF_4]^- \xrightarrow{BF_3} AgF_3$ (red solid) $+ KBF_4$

$2\,AgF_3 + Xe \longrightarrow 2\,AgF_2$ (Brown solid) $+ XeF_2$

PROPERTIES:

(i) Colorless crystalline solid and sublimes at 298 K.

(ii) Dissolves in water to give a solution with a pungent odour. Much soluble in HF liquid.

(iii) This is stored in a vessel made up of monel metal which is a alloy of nickel.

(iv) **Reaction with H_2 :** It reacts with hydrogen gas at 400^0C

$XeF_2 + H_2 \longrightarrow Xe + 2HF$

(v) **Hydrolysis :**

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

The above is neither a cationic hydrolysis nor an anionic hydrolysis as seen in ionic equilibrium. It is a covalent compound and hydrolysis is like that of PCl_5 .

(b) Hydrolysis is more rapid with alkali.

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

The reaction (a) is slower probably due to dissolution of XeF_2 in HF.

(vi) Oxidising properties :

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

The standard reduction potential for XeF_2 is measured to be + 2.64 V. Therfore it acts as a strong oxidising agent.

$$2e^- + 2H^+ + XeF_2 \longrightarrow Xe + 2HF;\ SRP = +2.64\ V$$

This oxidises halides to their respective halogens.

$$XeF_2 + 2\,HCl \longrightarrow Xe + 2\,HF + Cl_2$$

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

☞ In this manner XeF_2 will oxidise halide ions (except F^-) into free halogens.

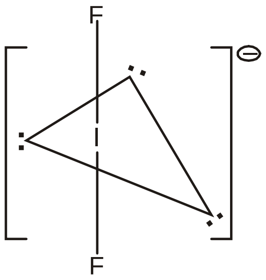
Similarly it can oxidise BrO_3^- (bromate) which are themselves good oxidising agents to BrO_4^- (perbromate ions) and Ce^{+3} to Ce^{+4} ion.

(vii) Oxidising as well as fluorinating properties :

It can act as strong oxidising agent as well as fluorinating agent.

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

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



hybridisation = sp^3d

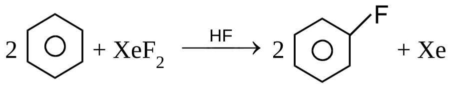
☞ F_3^- can not be formed as it has no d-orbitals to attain sp^3d hybridisation.

(viii) Reactions of XeF_2 + HF (anhydrous) :

$Pt + 3XeF_2 \xrightarrow{HF} PtF_6 + 3Xe$; $S_8 + 24\,XeF_2 \longrightarrow 8SF_6 + 24\,Xe$

$2CrF_2 + XeF_2 \longrightarrow 2CrF_3 + Xe$; $2MoO_3 + 6XeF_2 \longrightarrow 2MoF_6 + 6Xe + 3O_2$

$$Mo(CO)_6 + 3\,XeF_2 \longrightarrow MoF_6 + 3\,Xe + 6CO$$



$$8\,NH_3 + 3\,XeF_2 \longrightarrow N_2 + 6\,NH_4F + 3\,Xe$$

$$2NO_2 + XeF_2 \longrightarrow 2\,NO_2F + Xe$$

(nitronium fluoride)

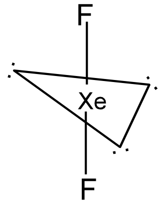
(ix) Formation of addition compounds : XeF_2 reacts with fluoride ion acceptors to form cataionic species and fluoride ion donors to form fluoroanions.

$$XeF_2 + PF_5 \longrightarrow [XeF]^+[PF_6]^-$$

IF_5 (lewis acid) + $XeF_2 \longrightarrow [XeF]^+[IF_6]^-$; $2SbF_5$ (lewis acid) + $XeF_2 \longrightarrow [XeF]^+[SbF_6]^-$

☞ Similar behaviour is shown by PF_5 and AsF_5

Structure : Shape linear and geometry trigonal bipyramidal.



hybridisation = sp^3d

(b) XENON TETRAFLUORIDE (XeF_4) :

PREPARATION:

$$\underset{1}{Xe} + \underset{5}{2F_2} \xrightarrow[\text{7 bar, Ni–tube}]{\text{873K,}} XeF_4$$

Xe : F_2 = 1 : 5

PROPERTIES:

(i) It is a colorless crystalline solid and sublimes at 298 K.

(ii) It undergoes sublimation, soluble in CF_3 COOH. It undergoes hydrolysis violently hence no moisture must be present during it's preparation.

(iii) **Reaction with H_2O :**

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

☞ XeO_3 is white solid and explosive compound (dry), soluble in water (well behaved in water)

☞ XeO_3 reacts with NaOH forming sodium xenate

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

☞ It disproportionates into perxenate ion in basic medium.

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

Xenic acid (H_2XeO_4) is a very weak acid.

(i) $[XeO]_6^{4-} \xrightarrow[\text{water}]{H^+} XeO_3 + O_2$ (slow decomposition)

(ii) $[XeO_6]^{4-} + Mn^{+2} \longrightarrow MnO_4^- + XeO_3$

$[XeO_6]^{4-}$ is obtainable as $Na_4\,XeO_6 \cdot 8H_2O$ (sodium perxenate)

(iv) **Oxidising properties of XeF_4 :**

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

(v) **Addition reactions :** XeF_4 reacts with fluoride ion acceptors to form cataionic species and fluoride ion donors to form fluoroanions.

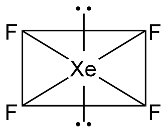
$$XeF_4 + SbF_5 \longrightarrow [XeF_3]^+\,[SbF_6]^-$$

(vi) **Fluorinating angen :**

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

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

Structure : Shape square planar & geometry octahedral



hybridisation = sp^3d^2

(c) XENON HEXAFLUORIDE (XeF_6) :

PREPARATION:

(i) $$\underset{1\ :\ 20}{Xe + 3F_2} \xrightarrow[\text{Ni–tube}]{573\,K,\ 60-70\,bar} XeF_6$$

(ii) $$XeF_4 + O_2F_2 \longrightarrow XeF_6 + O_2$$

PROPERTIES :

(i) Colourless crystalline solid and sublimes at 298 K.

(ii) It gives yellow liquid on melting where as other form white liquids on melting (a point of difference)

(iii) HF is a good solvent for all three fluorides.

(iv) **Hydrolysis :**

(a) Complete hydrolysis : $XeF_6 + 3H_2O \longrightarrow XeO_3$ (white solid) + 2HF

(b) Partial hydrolysis : $XeF_6 + H_2O \longrightarrow XeOF_4$ (colorless solid) + 2HF

(v) **Reaction with silica (SiO_2) :**

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

(vi) **Thermal decomposition (effect of heat) :**

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

☞ XeF_2 & XeF_4 do not undergo decomposition

(vii) **Formation of addition compounds :**

$$XeF_6 + SbF_5 \longrightarrow [XeF_5]^+[SbF_6]^- \ ; \qquad XeF_6 + BF_3 \longrightarrow [XeF_5]^+[BF_4]^-$$

(viii) **Reaction With H_2 :**

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

(ix) **Reaction of XeF_6 with XeO_3 :**

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

(x) **F^- donating/ F^- accepting properties :**

XeF_6 reacts with fluoride ion acceptors to form cataionic species and fluoride ion donors to form fluoroanions.

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

donation { $XeF_6 + PtF_5 \longrightarrow (XeF_5^+)(PtF_6^-)$

acceptance {

$\underset{\text{(alkali metal fluoride)}}{CsF} + XeF_6 \longrightarrow \underset{\text{(caesium heptafluoroxenate)}}{CsXeF_7}$

$2CsXeF_7 \longrightarrow XeF_6 + \underset{\text{(caesium octafluoroxenate)}}{Cs_2XeF_8}$

☞ **Order of oxidising power :**

$XeF_2 > XeF_4 > XeF_6$

STRUCTURE : Shape caped octahedral (distorted oactahedral)

(d) XENON–OXYGEN COMPOUNDS :

Hydrolysis of XeF_4 and XeF_6 with water gives XeO_3.

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

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

Partial hydrolysis of XeF_6 gives oxyfluorides, $XeOF_4$ and XeO_2F_2 .

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

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

XeO_3 is a colourless explosive solid and has a pyramidal molecular structure. $XeOF_4$ is a colourless volatile liquid and has a square pyramidal molecular structure.

Uses :

Helium is a non–inflammable and light gas. Hence, it is used in filling ballons for meterological observations. It is also used in gas–cooled nuclear reactors. Liquid helium (b.p.4.2 K) finds use as cryogenic agent for carrying out various experiments at low temperatures. It is used to produce and sustain powerful superconducting magnets which form an essential part of modern NMR spectrometers and Magnetic Resonance Imaging (MRI) systems for clinical diagnosis. It is used as a dilulent for oxygen in modern diving apparatus because of its very low solubility in blood.

Neon is used in discharge tubes and fluorescent bulbs for advertisement display purposes. Neon bulbs are used in botanical gardens and in green houses.

Argon is used mainly to provide an inert atmosphere in high temperature metallurgical process (arc welding of metals or alloys) and for filling electric bulbs. It is also used in the laboratory for handing substances that are air–sensitive.

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