21

MAIN GROUP ELEMETNS AND THEIR COMPOUNDS-II

21.1 INTORDUCTION

You have already studied the chemistry of some main group elements in the chapter main group elements and their compounds-I. We shall discuss in this chapter the remaining members of the main group : namely nitrogen, phosphorus, oxygen, sulphur, halogens and noble gases.

The compounds of the elements discussed in this chapter find numerous uses in daily life.

21.2 OBJECTIVES

After reading this lesson you will be able to

- recall the allotropic modifications of phosphorus.
- explain the difference in chemical reactivities of allotropes of phosphorus.,
- describe the composition, methods of preparation and properitics of different hydrides of nitrogen and phosphorus, (NH_3, N_2H_4, PH_3)
- describe the composition, properties and structures of various oxoacids of Nitrogen and Phosphorus (HNO_2, HNO_3 H_3, PO_3 and H_3PO_4)
- recognise the various reactions of nitric acid with different metals (Cu, Zn, Mg, Al) C, P, S, iodine and glycerine.

- describe the methods of preparation of oxides of S (SO_2, SO_3), their properties and structures.
- Write the structure of some of the oxo acids of sulphar (H_2SO_3, H_2SO_4)
- differenciate the role of H_2O_2, as an oxidising agent from reducing agent.
- draw the structure of H_2O_2
- desribe the preparation, properties and uses of H_2O_2
- explain : the gradation in the characteristics of halogens,
- describe the laboratory and industrial method of preparation of chlorine
- describe the methods of preparation and properties of hydracids of halogens (HF, HCl, HBr and HI)
- recognise the formation of simple binary compounds of xenon with most elcetronegative elements, i.e., Flourine and oxygen (XeF_2, XeF_4, XeF_6, XeO_3 and XeO_4)
- explain the structures of the compounds $Xe\ F_2$, $Xe\ F_4$, XeF_6, XeO_3 and XeO_4 on the basis of VSEPR theory.
- list the application of chloroflourocarbons and their role in causing depletion of ozone layer in the stratosphere.
- suggest replacement of chloroflourocarbons by environment friendly chemicals.

21.3 NITROGEN AND PHOSPHORUS

Nitrogen and phosphorus belong to the 15th group of the periodic table. Phosphorus is found in several allotropic forms both of which find several uses in different areas. Let us read about them.

21.3.1 Allotropic forms of phosphorus

Phosphorus exists in three allotropic modifications, namely white, red, and black phosphorus. These are discussed below:

White phosphorus is a soft yellow waxy solid. It contains P_4 units held tetrahedrally by van der waal's forces. Its m.p. is 317 K and boiling point is 553 K. It is toxic and ignites readily in air at 308 K. Therefore it has to be stored with care. It is soluble in carbon disulphide. Its density is 1.8 g cm^{-3}.

Sodium hydroxide solution when heated with white phosphorus gives phosphine (PH_3).

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

When white phosphorus is reacted wtih chlorine and heated it produces PCl_3 and PCl_5.

Red Phosphorus is formed when white phosphorus is heated in abscence of air at 543 K for several days. Its density is 2.2 cm^{-3} and it is a red brittle powder. Its melting point is 863 K (under pressure) and it sublimes at 673 K. It is non-toxic and is insoluble in carbon disulphide. Red phosphorus exists as a macromolecule. Red phosphorus does not react with sodium hydroxide. It does not react with chlorine unless heated.

Black Phosphorus can be prepared by heating white phosphorus to 473 K under high pressure and in the absence of air. It conducts electricity and resembles graphite.

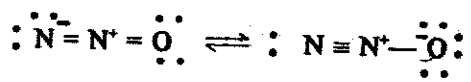
21.3.2 Composition of Oxides of Nitrogen

Nitrogen forms five types of oxides, however structure of only three is discussed here.

Name of oxide	Formula	Oxidation state of nitrogen
Dinitrogen oxide	N_2O	+1
Nitrogen oxide	NO	+2
Dinitrogen trioxide	N_2O_3	+3
Nitrogen dioxide	NO_2	+4
Dinitrogen pentoxide	N_2O_5	+5

Dinirogen oxide

It is a gas and its molecule has a linear structure which is a resonance hybrid of two forms.



Nitrogen oxide (Nitric oxide)

It is a colourless gas, virtually insoluble in water. It acts as a reducing agent. The structure of nitric oxide (NO) is given bellow :

N......O
|| ||
O......N

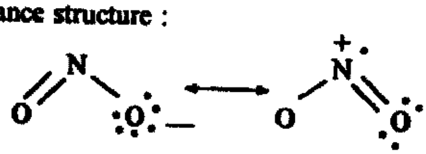
(dimer in liquid state)

Nitrogen dioxide (dinitrogen tetroxide)

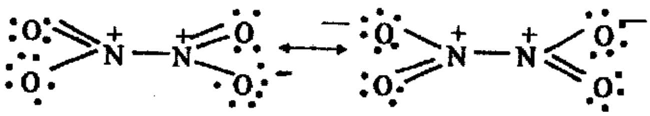
Nitrogen dioxide (NO_2) exists in equilibrium with its dimer N_2O_4.

$$N_2O_4\,(g) \underset{\text{cool}}{\overset{\text{heat}}{\rightleftharpoons}} 2NO_2(g) \underset{\text{cool}}{\overset{\text{heat}}{\rightleftharpoons}} 2NO\,(g) + O_2\,(g)$$

It has an angular resonance structure :



The planer dimer also shows resonance :



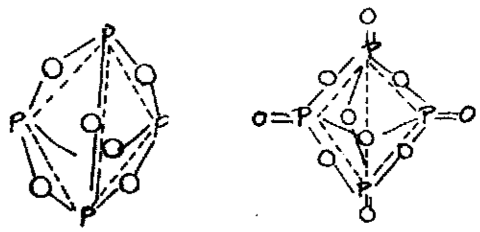
21.3.3 OXIDES OF PHOSPHORUS

Phosphorus forms two oxides :

(a) Phosphorus (III) Oxide P_4O_6

(b) Phosphorus (v) Oxide P_4O_{10}

The oxidation number of phosphorus in these oxides is +3 and +5 respectively. The phosphorus atom in these oxides is sp^3 hydridized. Phorphorus (III) oxide exists as dimer. In this structure, P_4 tetrahedral has oxygen atom bridging between two phosphorus atoms.



Phosphorus (v) oxide exists in a number of polymorphic forms, at least three of which are crystalline. It has a structure similar to P_4O_{16} except that each phosphorus atom is bonded to an extra oxygen. In addition phosphorus is found to expand its octet instead of datively bonding to oxygen using lone pair.

21.3.4 Hydrides of Nitrogen and Phosphorus

Nitrogen forms hydrides, two of which namely ammonia (NH_3) and hydrazine (N_2H_4) are well known. Phosphorus also forms an important hydride, phosphine (PH_3).

Preparations, properties and composition of the hydrides of nitrogen and phosphorus are discussed below:

Ammonia (NH_3) :

Preparation: In laboratory it can be prepared by heating ammonium chloride with slaked time.

$$2NH_4Cl + Ca(OH)_2 \xrightarrow{\text{heat}} CaCl_2 + 2H_2O + NH_3$$

It can also be prepared by hydrolysis of magnesium nitride.

$$Mg_3N_2 + 6H_2O \longrightarrow 3Mg(OH)_2 + 2NH_3$$

Properties : It is a colourless gas with pungent odour and highly is soluble in water.

Its aqueous solution is weakly basic due to the equilibrium:

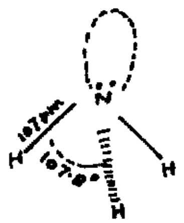
$$NH_3 + H_2O \rightleftharpoons NH_4OH$$

Oxidation of ammonia in presence of catalyst is given by reaction

$$4NH_3 + 5O_2 \xrightarrow{\text{Pt. catalyst}} 4NO + 6H_2O$$

Ammonium reacts with chlorine.

$$2NH_3 + 3Cl_2 \longrightarrow N_2 + 6HCl$$



Uses: Ammonia is used in the fertilizer industry, in the manufacture of nitric acid; in the manufacture of Na_2CO_3 and as a refrigerant.

Structure : Ammonia molecule is trigonal pyramidal with the nitrogen atom at the apex. The nitrogen atom is sp^3 hydridized in which one of the tetrahedral position is occupied by a lone pair.

Phosphine (PH_3) Phosphine is prepared:

Preparation: (a) By the action of calcium phosphide and water.

$$Ca_3P_2 + 6H_2O \longrightarrow 2PH_3 + 3Ca(OH)_2$$

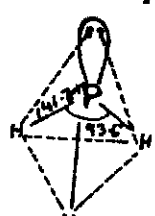
(b) By the action of white phosphorus and strong alkali.

$$P_4 + 3KOH + 3H_2O \longrightarrow PH_3 + 3KH_2PO_2$$

Properties : It is a poisonous gas. In the liquid state it is not associated via hydrogen bonds unlike NH_3. It is insoluble in water. It is a much weaker base than NH_3. It reacts with strong acids like HI

$$PH_3 + HI \longrightarrow PH_4I.$$

Structure : It is a covalent compound having pyramidal shape.



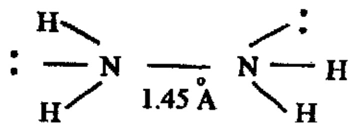
Hydrazine (N_2H_4)

Prreparation : It is prepared by oxidising NH_3 with NaOCl.

$$2NH_3 + NaOCl \longrightarrow N_2H_4 + NaCl + H_2O$$

Properties : It is strong reducing agent and is used as a rocket fuel. It decomposes violently when heated. The boiling point, 387 K, is high because of hydrogen bonding. It is a weak base in the presence of water, Its hydrates have the formulae $N_2H_4.H_2O$ and $N_2H_4(2H_2O)$,

Structure : Each nitrogen atom is tetraahedrally



surrounded by one N, two H and a lone pair. The molecule is capable of rotaing about its N-N bond and adopt a non-eclipsed conformation.

Uses:

Since hydrazine decomposes suddenly into gaseous form it is used as a rocket fuel. It is also used as reducing agent in laboratories.

21.3.5 Oxy Acids of Nitrogen

Nitrous Acid (HNO_2)

Preparation : Aqueous solution of nitrous acid (HNO_2) can be prepared by the action of nitrite salts with strong acid.

$$NaNO_2\ (aq) + HCl\ (aq) \longrightarrow NaCl\ (aq) + HNO_2\ (aq)$$

Composition :- molecular formula HNO_2, ratio of elements: H : N : O = 1 : 14 : 32) (by mass)

Properties :- 1. This is an unstable acid, fresh aqueous solutions are blue but slowly turn brown because of the following reaction:

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

$$2NO + O_2 \longrightarrow 2NO_2$$

3. Since nitrogen in HNO_2 is in an intermediate state, it can function either as an oxidizing agent or as a reducing agent.

a) **Reducing Property of HNO_2**

$$2KMnO_4 + 3H_2SO_4 + 5HNO_2 \longrightarrow K_2SO_4 + MnSO_4 + 3H_2O + 5HNO_3$$

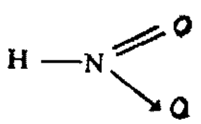
b) **Oxidising Property HNO_2 :**

$$2I + 2HNO_2 + 2H^+ \longrightarrow 2H_2O + 2NO + I_2$$

$$\underset{\text{Amine}}{R\text{-}NH_2} + HNO_2 \longrightarrow \underset{\text{Alcohol}}{R\text{-}OH} + N_2 + H_2O$$

Uses : It is used in manufacture of AZO dyes.

Structure :



Nitric Acid (HNO_3)

Preperation : In the laboratory, it can be prepased by heating $NaNO_2$ or KNO_2 with concentrated H_2SO_4 in glass retort and then vapours are condensed.

$$NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3$$

In industry it is manufactured by the catalytic oxidation of ammonia which involves the following reactions:

$$4NH_3 + 5O_2 \xrightarrow[\text{catalyst}]{\text{Pt/Rh}} 4NO + 6H_2O$$

$$2NO + O_2 \xrightarrow{1120K} 2NO_2$$

$$3NO_2 + H_2 \longrightarrow 2HNO_3 + NO$$

The aqueous nitric acid canbe concentrated by distillation followed by dehydration with Conc. H_2SO_4

Composition : Ratio of elements by mass: (H : N : O = 1 : 14 : 48)

Properties :

Physical : It is a colourless liquid. Its density at 298K is 1.504 g cm^{-3}

Chemical : (a) In aqueous solution, nitric acid is a strong acid and dissociates to give hydronium and nitrate ions.

$$H_2O + HNO_3 \longrightarrow H_3O^+ + NO_3^-$$

(b) It is neutralised by appropriate alkalies to yield nitrates.

$$NaOH + HNO_3 \longrightarrow Na\,NO_3 + H_2O$$

(c) On heating it gives NO_2

$$4HNO_3 \longrightarrow 4NO_2 + O_2 + 2H_2O$$

(d) It is a good oxidising agent and oxidizes with non metals:-

$$C + 4HNO_3 \longrightarrow CO_2 + 4NO_2 + 2H_2O$$

$$S + 6HNO \longrightarrow H_2SO_4 + 6NO_2 2H_2O$$

$$P_4 + 20HNO_3 \longrightarrow 4H_3PO_4 + 20NO_2 + 4H_2O$$

$$I_2 + 10HNO_3 \longrightarrow 2HIO_3 + 10NO_2 + 4H_2O$$

Reaction of HNO_3 with :- Cu, Zn, Mg, Al, C, P, S, I_2 & glycerine

(a) Reaction of HNO_3 with cu:

$$Cu + HNO_3 \xrightarrow[\text{(conc.)}]{} Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

$$3Cu + 8HNO_3 \xrightarrow[\text{(dil.)}]{} 3Cu(NO_3)_2 + 2NO + 4H_2O$$

(b) Reaction of HNO_3 with Zn:

$$Zn + 10HNO_3 \xrightarrow[\text{(dil.)}]{} 4Zn(NO_3)_2 + N_2O + 5H_2O$$

(c) Reaction of very dilute and cold nitric acid with magnesium.

$$Mg + 2HNO_3 \longrightarrow Mg(NO_3)_2 + H_2$$

(d) Reaction of HNO_3 with Al:

Aluminium loss its normal reactivity after being dipped in conc. HNO_3. This is due to formation of thin protective layer of the oxide on its surface which prevents further action.

(e) Reaction of HNO_3 with carbon :

$$C + 4HNO_3 \xrightarrow[\text{(conc.)}]{} H_2CO_3 + H_2O + 4NO_2$$

(f) Reaction of HNO_3 with Phoshorus:

$$P_4 + 20HNO_3 \longrightarrow 4H_3PO_4 + 20\ NO_2 + 4H_2O$$

(g) Reaction HNO_3 with Sulphur:

$$S + 6HNO_3 \longrightarrow H_2SO_4 + 6NO_2 + 2H_2O$$

(h) Reaction of HNO_3 with I_2 :

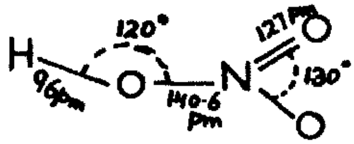
$$I_2 + 10HNO_3 \longrightarrow 10NO_2 + 2HIO_3 + 4H_2O$$

(i) Reaction of HNO_3 with Glycerine: (froms Nitroglycerine)

$$C_3H_5(OH)_3 + (HNO_3\ \text{conc.}\ H_2SO_4) \xrightarrow{\text{Nitration}} C_3H_5(NO_2)_3 + H_2O$$

Structure : In the gaseous state HNO_3 exists as a planar molecule with the structure:

Uses: It is used in the manufacture of Ammonium nitrate for fertlizers and other nitrates for use in explosive



21.3.6 Oxyacids of Phosphorus

Phosphorus acid (H_3PO_3)

Preparation: It is prepared by dissolving phosphorus trioxide in water

$$P_4O_6 + 6H_2O \longrightarrow 4H_3PO_3$$

Properties: (a) It is a colourless solid which melts at 346K.

(b) It gives PH_3 on heating. $4H_3PO_3 \xrightarrow{573K} 3H_3PO_4 + PH_3$

(c) It reduces Hg^{2+} to Hg^+.

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

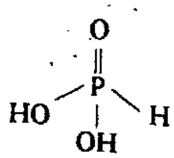
(d) It is a diabasic acid and fofms two series of salts, hypo phosphite and phosphites

$$H_3PO_3 + H_2O \rightleftharpoons H_3O^+ + H_2PO_3$$

$$H_3PO_3 + H_2O \rightleftharpoons H_3O^+ + HPO_3^{2-}$$

Uses: Phosphorus acid is used as a reducing agent and for the preparation of phophites.

Structure: The hydrogen directly linked to phosphorus is responsible for its reducing property.



Phosphoric Acid (H_3PO_4)

Preparation: It can be prepared by dissolving phosphorus pentoxide in hot water.

$$P_4O_{10} + 6H_2O \longrightarrow 4H_3PO_4$$

Properties:- (i) Pure phosphoric acid is crystalline solid; m.p; 315K; readily absorbs water.

(ii) On heating it first forms pyrophosphoric acid ($H_4P_2O_7$)and then metaphosphoric acid (HPO_3)

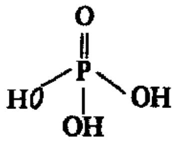
$$2H_3PO_4 \xrightarrow{520K} H_4P_2O_7 + H_2O$$

$$2H_3PO_4 \xrightarrow{870K} 2HPO_3 + H_2PO_4$$

(iii) It is a tribasic acid and forms three series of salts (phosphates PO_4, hydrogenphosphate HPO_4^{--}, and dihydrogen phosphate $H_2PO_4^-$)

Uses: It is used in the manufacture of phosphate fertilizers.

Struture of H_3PO_4



INTEXT QUESTIONS 21.1

1. Which isotope of phosphorus resembles graphite

 ....

2. Which oxide of nitrogen is called laughing gas.

 ....

3. Complete the following equations by filling blanks.

 (a) $C_3H_5(OH)_3 + 3HNO_3 \xrightarrow{\text{Conc. } H_2SO_4} 3H_2O +$ ....

 (b) $6HNO_3 + S \longrightarrow H_2SO_4 + 2H_2O +$ ....

 (c) $HNO_3 + Zn \longrightarrow Zn(NO_3)2 + 5H_2O +$ ....

 (d) $4NH_3 + 5O_2 \longrightarrow \xrightarrow{Pt/Rh} 4NO +$ ....

 (e) $4H_3PO_3 \xrightarrow{573} 3H_3PO_4$ ....

 ....

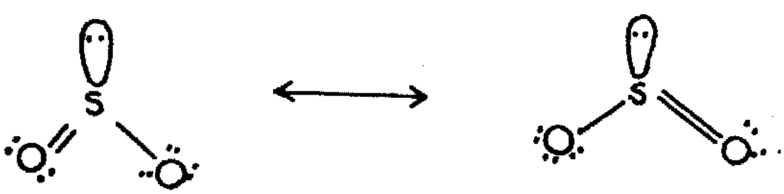
21.4 OXYGEN AND SULPHUR

Oxygen and sulphur belong to 16th group of the periodic table. Let us learn about some of the compounds of oxygen and sulphur.

Sulphur dioxide (SO_2) Sulphur forms two important oxides; SO_2 and SO_3. Sulphur dioxide (SO_2) is a pungent smelling colourless gas, soluble in water. Moisture converts it to sulphurous acid which is very corrosive.

Structure and Composition :

Suphur dioxide is a bent molecule having a bond angle of 119.5°. Resonating structures of sulphur dioxde are given below:



Preparations

Sulphur dioxide is prepared by burning pure sulphur in oxygen in proper mole ratio. Allernatively, sulphur dioxide can be prepared by any one of the following reactions:

$$Cu\ (s)\ +2H_2SO_4(l) \longrightarrow CuSO_4(aq) + SO_2\ (g) + 2H_2O\ (l)$$

$$S\ (s) + 2H_2SO_4\ (l) \longrightarrow 3SO_2\ (g) + 2H_2O\ (l)$$

$$2HBr\ (aq) + H_2SO_4\ (aq) \longrightarrow Br_2(l) + SO_2\ (g) + 2H_2O\ (l)$$

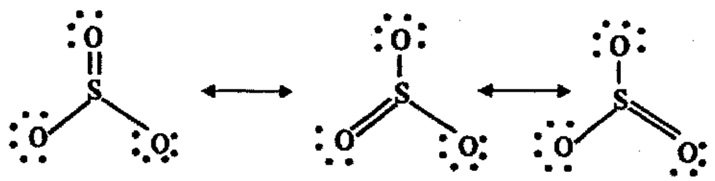
Properties : Sulphurdioxide is a weak reducing agent and it self gets oxidized.

$$2SO_2\ (g) + O_2\ (g) \xrightarrow{V_2O_5} 2SO_3\ (g)$$

$$SO_2\ (g) + Cl_2(g) \longrightarrow SO_2Cl_2\ (l)$$

Structure Sulphur trioxide (SO_3)

Sulphur trioxide in vapour state is a monomeric molecule with the sulphur atom at the centre of an equilateral triangle, while the oxygen atoms occupy the corners of the triangle. The electronic structure of sulphur trioxide, (SO_3) is a resonance hybrid of the different lewis structures:



Properties: Sulphur trioxide reacts with water to form sulphuric acid.

$$SO_3 + H_2O \longrightarrow H_2SO_4.$$

SO_3 reacts with barium oxide to give barium sulphate.

$$BaO + SO_3 \longrightarrow BaSO_4$$

When heated to a high temperature, SO_2 is produced.

$$2SO_3 \xrightarrow{1173\ K} 2SO_2 + O_2$$

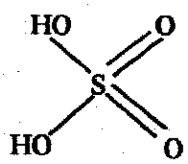
(ii) Oxo-acid of sulphur

SULPHURIC ACID, H_2SO_4 **(Tetraoxosulphate (vi) acid)** sulphuric acid is a thick syrupy transparant liquid. The acid is considered to be king of chemicals and is one of the most important chemical for industry. It is a very corrosive substance. It is prepared by oxidizing sulphur to sulphur dioxide and then to trioxide in the presence of catalyst vanadium (v) oxide. The trioxide of sulphur is dissolved in sulphuric acid producing oleum, ($H_2S_2O_7$). Oleum is diluted with water to get the requird concentration of sulphuric acid.

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

$$SO_3 + H_2SO_4 \longrightarrow H_2S_2O_7 \text{ (Oleum)}$$
$$H_2S_2O_7 + H_2O \longrightarrow 2H_2SO_4$$

Structure of Sulphuric Acid



Dehydrating Properties :

In aqueous media sulphuric acid displays its dibasic character. The strong affinity for water makes this acid a strong dehydrating agent.

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

Acidic Properties: Sulphric acid reacts with water to give solutions which give the reactions of strong acids.

$$H_2SO_4 + H_2O \longrightarrow HSO_4^- + H_3O^+ \text{ (aq)}$$
$$HSO_4^- + H_2O \longrightarrow H_3O^+ \text{ (aq)} + SO_4^-$$

Thus we see two series of salts are formed.

$$H_3O^+ + OH^- \longrightarrow H_2O$$

Oxidising Properties:

Hot sulphuric acid functions as an oxidising agent.

$$3H_2S(g) + H_2SO_4(l) \longrightarrow 4H_2O(l) + 4S(s)$$
$$C\ (s) + H_2SO_4(l) \longrightarrow 2H_2O\ (l) + CO_2(g) + 2SO_2(g)$$
$$S\ (s) + 2H_2SO_4\ (l) \longrightarrow 2H_2O\ (l) + 3SO_2(g)$$

A variety of metals react with the acid reflecting the oxidizing power of the acid

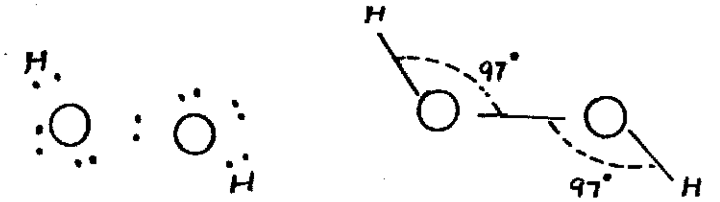
$$2HBr + H_2SO_4 \longrightarrow 2H_2O + SO_2 + Br_2$$
$$8HI + H_2SO_4 \longrightarrow 4H_2O + H_2S + 4I_2$$
$$Cu\ (s) + 2H_2SO_4(l) \longrightarrow CuSO_4(aq) + 2H_2O + 2SO_2(g)$$
$$Zn\ (s) + 2H_2SO_4\ (l) \longrightarrow ZnSO_4\ (aq) + 2H_2O\ (l) + 2SO_2\ (g)$$

Displacement Reactions :

$$NO_3^- + H_2SO_4 \longrightarrow HSO_4^- + HNO_3$$
$$Cl^- + H_2SO_4 \longrightarrow HCl + HSO_4^-$$

(iii) Hydrogen Peroxide :

Structure : The lewis structure and molecular structure of hydrogen peroxide are given below:



The charge on the peroxide ion is – 2. The peroxide ion is strongly basic ion.

Preparation: Hydrogen peroxide can be prepared by the following reactions:

(i) $Ba_2O_2 + H_2SO_4 \longrightarrow BaSO_4 + H_2O + H_2O_2$

(ii) $Na_2O_2 + 2H_2O \longrightarrow 2Na^+ + 2OH^- + H_2O_2$

(iii) Electrolysis of sulphuric acid in presence of NH_4HSO_4.

$2H_2SO_4 \xrightarrow{\text{Electrolysis}} H_2S_2O_8 + H_2$

$H_2S_2O_8 + 2H_2O \longrightarrow 2H_2SO_4 + H_2O_2$

Sulphuric acid produced is recycled.

(iv) By reduction of 2-ethy1 anthraquimone.

$C_{16}H_{12}O_2 + H_2 \xrightarrow{\text{Pd catalyst}} C_{16}H_{12}(OH)_2$

$C_{16}H_{12}(OH)_2 + O \longrightarrow C_{16}H_{12}O_2 + H_2O_2$.

Concentrations: In general hydrogen peroxide is produced in varied concentration. When hydrogen peroxide reaches a concenration of about 0.15 mole per litre it is extracted with water to produce higher concentration to the extent of 20%. It can be further concentrated by vacuum distillation, temperature has to be kept low as hydrogen peroxide decomposes at higher temperatures. Very pure hydrogen peroxide is quite stable. In routine applications, hydrogen peroxide of 90% concentrations is used. Hydrogen peroxide needs a stabilizer when it is to be stored.

Properties: Pure hydrogen peroxide is a clourless syrupy liquid and has sharp odour. It has a boiling point of 423K. It is miscible in all proportions with water, alcohol and ether.

(i) It is thermally unstable

$2H_2O_2 \longrightarrow 2H_2O + O_2$

(ii) It acts as an oxidizing agent due to its ability to lose oxygen easily.

$H_2O_2 \longrightarrow H_2O + O$

It oxidizes sulphurus acid (H_2SO_3) to sulpuric acid, H_2SO_4

$H_2SO_3 + H_2O_2 \longrightarrow H_2SO_4 + H_2O$.

Sulphides are oxidized to sulphates

$PbS + 4H_2O_2 \longrightarrow PbSO_4 + H_2O$

iii) As a reducing agent it reduces silver oxide to metallic silver.

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

Similarly, chlorine is reduced to chloride ion.

$Cl_2\,(g) + H_2O_2\,(aq) + 2H_2O(l) \longrightarrow O_2\,(g) + 2H_3O^+(aq) + Cl^-(aq)$

iv) Oxides of mercury, gold and platinum can be reduced. Agents like MnO_2 and $KMnO_4$ are also reduced.

$6H_3O^+ + 2MnO_4 + 5H_2O_2 \longrightarrow 5O_2 + 2Mn_2{}^{2+} + 14H_2O.$

v) With basic compounds it shows acidic character.

$Ba^{2+}(aq) + 2OH^-(aq) + H_2O_2(l) \longrightarrow BaO_2(aq) + 2H_2O\,(l)$

Uses:

(i) It is used as a bleaching and antiseptic agent.

(ii) It is disinfectant and germicide.

(iii) It is used as an oxidizing agent and is now being used for pollution control e.g., treatment of drainage and sever for dechlorination.

INTEXT QUESTION 21.2

1. Mark T for true and F for false statements.
   (i) Oleum is formed when sulphur trioxide is passed through concentrated sulphuric acid.
   (ii) Sulphuric acid is a dehydrating agent.
   (iii) Sulphuric acid is a dibasic acid.
   (iv) Sulphuric acid is a strong oxidising agent.
   (v) Hydrogen Sulphide is oxidized to sulphur by sulphuric acid.

   ....

2. Write a reaction showing reducing property of sulphur dioxide.

   ....

3. "Hydrogen peroxide can be used as an oxidizing agent". Write one equation to prove the statement.

   ....

4. Write a chemical equation to show that hydrogen peroxide decomposes on long standing.

   ....

21.5 HALOGENS

(i) Gradation in the characteristics of Halogens :

All members are non-metals and show similarities amongst its members. Halogens are placed in group 17 of the periodic table.

Symbol	configuration
F	[He] $2S^2 2P^5$
Cl	[Ne] $3s^2 3p^5$
Br	[Ar] $3d^{10}\ 4s^2\ 4P^5$
I	[Kr] $4d^{10}\ 4s^4\ 4P^5$
At	[Xe] $4F^{14}\ 5d^{10}\ 6s^2\ 6P^5$

Except fluorine all show variable oxidation states. Fluorine differs from other members of the group because its size is very small as compared to other members. Thus it holds the electrons more firmly. Moreover fluorine lacks low lying d-orbitals which may be used for bonding.

The electropostive character increases as we go down the group. All elements of the group exist as diatomic molecules and are all coloured. Gaseous F_2 is light yellow, Cl_2 is greenish yellow, Br_2 exists as gas and as liquid in dark red brown colouration, iodine gas is violet but its solid crystals are very dark violet in colour. The colours of the elements depend upon their ability to absorb light on promoting an electron from the ground state to a higher state.

(ii) Structure and nature of halogens

The elements of the halogen group are one short of the octet in their valence shell. Fluorine, Chlorine, bromine and iodine exhibit -1 oxidation state. Other oxidation states are also shown by some of the hologens. Halogens also react with other halogens to form interhalogens, for example, ClF_3, BrF_3, ICl, BrF_5, IF_5 and IF_7.

Halogens form hydracids with hydrogen; HF, HCl, HBr, HI, which show increasing strength as we go down the group, i.e., HI is the strongest acid.

Fluorine react with noble gases and forms a number of compounds, particularly with Xenon, i.e., XeF_2, XeF_4 and XeF_6 . The geometries of these compounds are now established, XeF_2 is linear, XeF_4 is square planar and XeF_6 is a distorted octahedron.

(iii) Hydracids of Halogens

The haloacids under consideration are HF, HBr and HI. The bond distance increases with the size of the halogen. The bond also becomes more ionic. Since the bond length increases and becomes more ionic, the ease with which the acid looses hydrogen ion increases. Thus the acidic strength of the acids increases in the order. $HF < HCl < HBr < HI$.

21.5.1 Preparation of Acids

Industrially HF is made by heating CaF_2 with strong H_2SO_4.

$$CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 2HF$$

HCl is made from salt cake:

$$NaCl + H_2SO_4 \xrightarrow{423\ K} HCl + NaHSO_4$$
$$NaCl + NaHSO_4 \xrightarrow{823\ K} HCl + Na_2So_4$$

Phosphoric acid is used to make HI

$$H_3PO_4 + NaI \longrightarrow HI + NaH_2PO_4$$

HBr is made by a similar method. Also we use red phosphorus for making HBr & HI

$$2P + 3Br_2 \longrightarrow 2PBr_3 \xrightarrow{6H_2O} 6HBr + 2H_3PO_3$$
red
$$2P + 3I_2 \longrightarrow 2PI_3 \xrightarrow{6H_2O} 6HI + 2H_3PO_3$$

21.5.2 Properties of the acids

For making Freons

$$CCl_4 + 2HF \xrightarrow[\text{(anhydrous)}]{SbCl_5} CCl_2F_2 + 2HCl$$
$$B_2O_3 + 6HF \xrightarrow{\text{conc. } H_2SO_4} 2BF_3 + 2H_2SO_4 + H_2O$$
$$Al_2O_3 + 6HF \longrightarrow 2AlF_3 + 3H_2O$$
$$HCl + H_2O \longrightarrow (H_3O)^+ + Cl^-$$

HBr and HI also demonstrate their strength by getting fully ionised. HF experiences extensive H-bonding due to very high eletronegativity of fluorine. HF is slightly ionised in water.

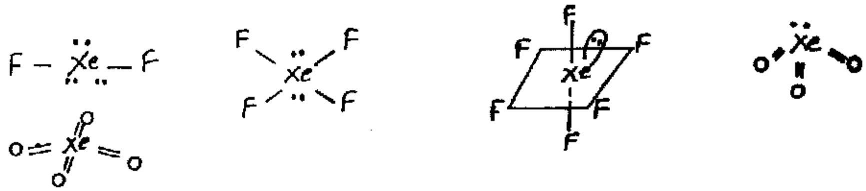
$$2HF \rightleftharpoons [H_2F]^{+1} + F^-$$

21.6 COMPOUNDS OF NOBLE GASES

The elements of group 18 are termad as "Noble Gases" The electronic configuration of atoms of these elements show completed shells (ns^2, np^6). All the available and admissible orbitals are fully occupied. Thus there are no electrons that are left unshared or available for bonding. These elements therefore show lack of chemical reactivity.

However, if certain energy field is applied to xenon (xenon has minimum ionization energy amongst noble gases) in an electric tube, the atoms get polarised to one side and then to the other. During this polarization the atom develops a dipole for a short span of time. The fluorine atoms (being most electronegative) get immediately attracted to the polarised atom and thus make a bond.

Fluorine and oxygen react with Xenon under suitable reaction conditions and forms certain compounds. e.g., XeF_2, XeF_4, XeF_6, XeO_3, and XeO_4. The shapes of these molecules decribed below can be explained in terms of VSEPR discussed in the chapter :"chemical bond"



The first stable compound of Xenon with fluorine was XeF_4. The compound was made by mixing Xenon gas and fluorine gas at 673K for one hour and then cooling to 195K. The substance formed is colourless and crystalline having melting point 363K and is stable under normal conditions. The Xe-F bonds are weak as compared to other normal bonds.

Xenon compounds show strong tendencies as oxidizing agents and disproportionates in water. Xenon compounds react with strong lewis acids by donating fluoride ion. Few examples are given below:

$$2XeF_2 + 2H_2O \longrightarrow 2Xe + 4HF + O_2$$

$$6XeF_4 + 8H_2O \longrightarrow 2XeOF_4 + 4Xe + 16HF + 3O_2$$

$$6XeF_4 + 12H_2O \longrightarrow 2XeO_3 + 4Xe + 24HF + 3O_2$$

In the second and third equations above you can see that the reactants are the same but the stoichiometries of the reactants are different giving rise to different products.

XeO_3 solid, in the dry state is a highly explosive compound.XeF_6 also reacts with water where Xenon shows +6 oxidation state, the products being the sensitive explosive XeO_3 and hydrogen fluoride.

$$XeF_6 + 6H_2O \longrightarrow XeO_3 + 6HF$$

Further reactions of XeF_6 and XeO_3 in alkaline medium show formation of per Xenate ions $XeO_6{}^{4-}$

In the electrochemical series xenon is placed below hydrogen indicating that Xenon is more suscptible to reduction than hydrogen ion.

In acidic medium :

$$XeO_3 + 6H^+ + 6e^- \longrightarrow Xe + 3H_2O, \quad E° = 1.8V$$

$$XeO_6 + 2H^+ + 2e^- \longrightarrow XeO_3 + 3H_2O, \quad E° = 3.0V$$

In basic medium

$$HXeO^{-4} + 3H_2O + 6e^- \longrightarrow Xe + 7OH^-, E° = 0.9V$$

$$HXeO^{3-} + 2H_2O + 2e^- \longrightarrow HxeO^{-4} + 4OH, \quad E° = 0.9V$$

> The structure of XeF_2 is linear XeF_4 is square planar and XeF_6 has a distorted octahedral structure.

21.6.1 Applications of Noble Gases

1. Helium is used in filling balloons.

2 Its mixture with oxygen is used by deep sea divers for breathing because of the rapid diffusion and lightness of helium, which reduces the muscular effort in breathing.

3 Helium provides inert atmosphere for reactions.

4 In liquified form it is used in cryogenic research.

5 Neon gas used in signs and lamps giving brilliant orange red glow, even through fog. Argon is filled in electric bulbs because it is chemically inert and has low heat of conductivity. The tungsten filament of the electric bulb gets a long life as its vapourization is prevented by the gas. Fluorescent tubes, like electric bulbs also have argon filled in them in addition to mercury vapour which adds to the glow. Krypton-Xenon mixture is used for filling flash bulbs for photography

21.6.2 Chlorofluoro carbons (CFC)

Chlorofluoro carbons are the compounds of carbon where chlorine and fluorine are substituted for hydrogen in saturated hydrocarbons. These compounds have very high capacity to retain heat. It is believed that the capacity to retain heat is about 10,000 times more than that of carbon-dioxide. Thus these molecles are capable of cooling other systems by taking away their heat.

Chlorofluoro carbons are also termed as **halons**. About 5 thousand metric tonnes of CFC's are still being produced in our country. In addition to their usage as aerosols, solvents, foam blowing agents and referigerants, they are also known to cause environmental hazard. CFC react with protective ozone layer in the stratosphere, thus causing perforation through which radiations from outer sphere might be entering our atmosphere and causing damage on our life systems. The destruction of ozone layer is termed as **ozone depletion** and is creating a ozone hole.

INTEXT QUESTIONS 21.3

1. Name the most electronegative hologen.

   ....

2. Name the halogen that can react with a inert gas.

   ....

3. Write a chemical reaction used for the laboratory preparation of Chlorine.

   ....

4. Arrange the hydracids in the decreasing order of their strength.

   ....

5. What group of carbon compounds is supposed to cause ozone depletion.

   ....

21.7 WHAT YOU HAVE LEARNT

- In group 15 of periodic table Nitrogen and phosphorus are non-metals. The metallic character increases down the group.
- Nitrogen is not capable of expanding its octet thus NCl_5 cannot be formed but all other memebers of the group are capable of doing that.
- Hydrides of nitrogen and phosphorus such as NH_3, N_2H_4 and PH_3 show important properties.
- Oxyacids of nitrogen (HNO_2, HNO_3) and phosphorus (H_3PO_3 and H_3PO_4) are formed which show a variety of reactions with metals and non-metals. Reactions of metals with HNO_3 are of great significance
- Oxygen and sulphur are non-metals of group number 16. Oxygen exists as diatomic molecule while sulphur exist as S_8 molecules. Both these elements form divalent anions however sulphur shows +4 and +6 oxidation state.
- Both the elements H and S, form hyd rides: H_2O and H_2O_2, H_2S. Water is liquid due to hydrogen bonding. Sulphur forms two oxides : SO_2 and SO_3 both the oxides are acidic in nature. Sulphur also forms a variely of oxoacids: $H_2 SO_3$, H_2SO_4, $H_2S_2O_7$ and $H_2S_2O_8$.
- Sulphuric acid displays strong and character and possess oxidizing and dehydrating properties.
- Halogens are placed in group number 17 of the periodic table. Flourine, Chlorine, Bromine, Iodine and Astotine are its members. All members of the group are very reactive They show variable oxidation state. Halogens react with other Halogen forming interhalogens. Halogen (Fluorine) can even react with noble gases. Halogens react with hydrogen forming hydracids. Fluoro-chloro-carbons are called halones which decompose ozone and are therefore environmentaly hazardous.
- Helium, xeon, arogon, krypton, and radon are the members of group number 18 and are collectively called inert gases.

  Xenon is known to react with fluorine to form XeF_2, XeF_4 and XeF_6.

20.8 TERMINAL EXERCISE

1. Write electron dot structures of the following:

   (a) Oxides of nitrogen, phosphorus and sulphur.

   (b) Hydrides of halogens.

   (c) H_2SO_4, HNO_3 and XeF_6.

   ....

2. Give reason why PF_5 is known and NF_5 is not.

   ....

3. Write the reactions in sequence showing the formation of sulphuric acid by contact process. Start with sulphur.

   ....

4. Write the reactions of fluorides of Xenon with water (any two).

   ....

5. Name the theory that justifies the shapes of the fluorides of Xenon.

   ....

6. Write chemical reactions that are likely to take place, when the following are mixed.
   (i) Magnisium nitride with water.
   (ii) Ammonia is reacted with excess of chlorine.
   (iii) Calcium phosphide with water
   (iv) Ammonia with NaOcl
   (v) Amine with Nitrous acid
   (vi) Carbon with nitric acid.
   (vii) Iodine with nitric acid.
   (viii) Magnesium with very dilute HNO_3.
   (ix) Glycrine with nitric acid.
   (x) Sulphur dioxide with phosphours (v) chloride.

CHECK YOUR ANSWERS

INTEXT QUESTION 21.1

1. Black phosphorus.
2. N_2O
3. (a) $C_3H_5(NO_3)$
   (b) SO_2
   (c) N_2O
   (d) NO
   (e) PH_3

INTEXT QUESTION 21.2

1. (i) T, (ii) T, (iii) T, (iv) T, (v) T,
2. $SO_2 + Cl_2 \longrightarrow SO_2Cl_2$

3. $H_2O_2 + NO \longrightarrow H_2O + NO_2$

4. $H_2O_2 \longrightarrow H_2O + O$

INTEXT QUESTION 21.3

1. Flourine
2. Flourine
3. $MnO_2 + 14HCl \longrightarrow MnCl_2 + H_2O + Cl_2$
4. HI > MBr > HCl > HF
5. Chlorofluorocarbons.

TERMINAL EXCERCISE

1. (a), (b), (c), see text.
2. Nitrogen cannot expand its octet because it has no 'd' orbitals.
3. $S + O_2 \longrightarrow SO_2$

   $SO_2 + O_2 \xrightarrow{V_2O_5} SO_3$

   $SO_3 + H_2SO_4 \longrightarrow H_2S_2O_7$

   $H_2S_2O_7 + H_2O \longrightarrow 2H_2SO_4.$
4. $XeF_6 + 6H_2O \longrightarrow XeO_3 + 6HF$

   $6XeF_4 + 8H_2O \longrightarrow 2XeOF_4 + 4Xe + 16HF + 3O_2$
5. VSEPR
6. (i) $Mg_3N_2 + 6H_2O \longrightarrow 3Mg(OH)_2 + 2NH_3$

   (ii) $2NH_3 + 3Cl_2 \longrightarrow N_2 + 3HCl$

   (iii) $Ca_3P_2 + 6H_2O \longrightarrow 3PH_3 + 3Ca(OH)_2$

   (iv) $NH_3 + NaOCl \longrightarrow N_2H_4 + NaCl + H_2O$

   (v) $RNH_2 + HNO_2 \longrightarrow R\text{–}OH + N_2 + H_2O$

   (vi) $C + 4HNO_3 \longrightarrow CO_2 + 4NO_2 + 2H_2O$

   (vii) $I_2 + 10HNO_3 \longrightarrow 2HIO_3 + 10NO_2 + 4H_2O$

   (ix) $3HNO_3 + C_3H_5(OH)_3 \xrightarrow{\text{conc. } H_2SO_4} 3H_2O + C_3H_5(NO)_3$

   (x) $SO_2 + PCl_5 \longrightarrow SOCl_2 + POCl_3$