

## CHAPTER-07

## P-Block Elements

## LECTURE-1

**GROUP-15 ELEMENTS:**

Group 15 includes nitrogen, phosphorus, arsenic, antimony, and bismuth. Nitrogen and phosphorus are non-metals, arsenic and antimony are metalloids and bismuth is a typical metal.

**Occurrence :**

- (i) Molecular nitrogen is 78% by volume of the atmosphere. In the earth's crust, it occurs as sodium nitrate ( $\text{NaNO}_3$  called Chile saltpeter) and potassium nitrate (Indian saltpeter).
- (ii) Phosphorus occurs in minerals of the apatite family,  $\text{Ca}_9(\text{PO}_4)_6 \cdot \text{CaX}_2$  ( $\text{X} = \text{F}, \text{Cl}$  or  $\text{OH}$ ) (e.g., fluorapatite  $\text{Ca}_9(\text{PO}_4)_6 \cdot \text{CaF}_2$ ) which are the main components of phosphate rocks?
- (iii) Arsenic, antimony, and bismuth are found mainly as sulfide minerals.

**Electronic Configuration:**

The valence shell electronic configuration of these elements is  $ns^2np^3$ . The  $s$ -orbital in these elements is 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 increases 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 filled  $d$  and/or  $f$  orbitals in heavier members.

**Ionization Enthalpy:**

Ionization enthalpy decreases down the group due to a gradual increase in atomic size. Because of the extra stable half-filled electronic configuration and smaller size, the ionization enthalpy of the group 15 elements is much greater than that of group 14 elements in the corresponding periods. The order of successive ionization 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 less.

**Physical Properties:**

- (i) All the elements of this group are polyatomic. Dinitrogen is a diatomic gas while all others are solids.
- (ii) Metallic character increases down the group. This is due to a decrease in ionization enthalpy and an increase in atomic size.
- (iii) The boiling points, in general, increase from top to bottom in the group but the melting point increases up to arsenic and then decreases up to bismuth.

(iv) Except for nitrogen, all the elements show allotropy.

### Chemical Properties:

#### Oxidation states and trends in 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 due to an increase in size and metallic character. Thus bismuth hardly forms any compound in  $-3$  oxidation state.
- The stability of the  $+5$  oxidation state decreases down the group. The only well-characterized Bi (V) compound is  $\text{BiF}_5$ .
- The stability of the  $+5$  oxidation state decreases and that of  $+3$  state increases (due to the inert pair effect) down the group.
- Nitrogen exhibits  $+1$ ,  $+2$ ,  $+4$  oxidation states when it reacts with oxygen.
- Phosphorus 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,  
$$3\text{HNO}_2 \rightarrow \text{HNO}_3 + \text{H}_2\text{O} + 2\text{NO}$$
- Similarly, in the case of phosphorus nearly all intermediate oxidation states disproportionate into  $+5$  and  $-3$  both in alkali and acid.
- However, the  $+3$  oxidation state in the case of arsenic, antimony, and bismuth becomes increasingly stable concerning 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  $\text{PF}_6^-$

#### Anomalous Properties of Nitrogen:

- Nitrogen differs from the rest of the members of this group due to its small size, high electronegativity, high ionization enthalpy, and non-availability of  $d$  orbitals.
- Nitrogen has a unique ability to form  $p\pi-p\pi$  multiple bonds with itself and with other elements having a small size and high electronegativity (e.g., C, O).
- Heavier elements of this group do not form  $p\pi-p\pi$  bonds due to the large size of atomic orbitals. Thus, nitrogen exists as a diatomic molecule with a triple bond (one  $s$  and two  $p$ ) between the two atoms. Consequently, its bond enthalpy ( $941.4 \text{ kJ mol}^{-1}$ ) is very high.
- On the contrary, phosphorus, arsenic, and antimony form single bonds as  $\text{P-P}$ ,  $\text{As-As}$ , and  $\text{Sb-Sb}$ .
- While bismuth forms metallic bonds in the elemental state. However, the single  $\text{N-N}$  bond is weaker than the single  $\text{P-P}$  bond because of the high interelectronic repulsion of the non-bonding electrons. The repulsion is due to the small bond length. As a result, the catenation tendency is weaker in nitrogen.
- Another factor that affects the chemistry of nitrogen is the absence of  $d$  orbitals in its valence shell. Besides restricting its covalency to four, nitrogen cannot form the  $p\pi-p\pi$

bond as the heavier elements can e.g.,  $R_3P = O$  or  $R_3P = CH_2$  ( $R = \text{alkyl group}$ ). Phosphorus and arsenic can form a  $p\pi-p\pi$  bond also with transition metals when their compounds like  $P(C_2H_5)_3$  and  $As(C_6H_5)_3$  act as ligands.

**Reactivity towards hydrogen:**

- (i) All the elements of Group 15 form hydrides of the type  $EH_3$  where  $E = N, P, As, Sb$  or  $Bi$ .
- (ii) 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.
- (iii) 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  $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$ .

**Reactivity to towards Oxygen:**

- (i) All these elements form two types of oxides:  $E_2O_3$  and  $E_2O_5$ .
- (ii) The oxide in the higher oxidation state of the element is more acidic than that of a lower oxidation state.
- (iii) Their acidic character decreases down the group. The oxides of the type  $E_2O_3$  of nitrogen and phosphorus are purely acidic.
- (iv) Oxide of arsenic and antimony are amphoteric and those of bismuth predominantly basic.

**Reactivity towards halogens:**

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

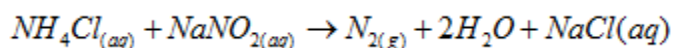
**(iv) Reactivity towards metals:**

All 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).

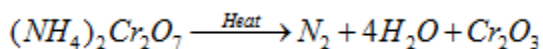
## LECTURE-2

**PREPARATION OF DINITROGEN:**

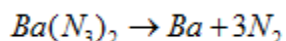
- i) Dinitrogen is produced commercially by the liquefaction and fractional distillation of air. Liquid dinitrogen (b.p. 77.2 K) distills out first leaving behind liquid oxygen (b.p. 90 K).
- ii) In the laboratory, dinitrogen is prepared by treating an aqueous solution of ammonium chloride with sodium nitrite.



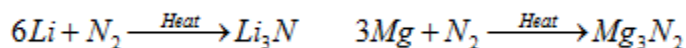
Small amounts of NO and HNO<sub>3</sub> are also formed in this reaction; these impurities can be removed by passing the gas through aqueous sulphuric acid containing potassium dichromate. It can also be obtained by the thermal decomposition of ammonium dichromate.



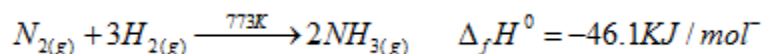
Very pure nitrogen can be obtained by the thermal decomposition of sodium or barium azide.

**Properties:**

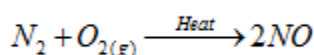
- i) Dinitrogen is a colorless, odorless, tasteless, and non-toxic gas.
- ii) The nitrogen atom has two stable isotopes: <sup>14</sup>N and <sup>15</sup>N. It has very low solubility in water (23.2 cm<sup>3</sup> per liter of water at 273 K and 1 bar pressure) and low freezing and boiling points.
- iii) Dinitrogen is rather inert at room temperature because of the high bond enthalpy of N≡N bond. Reactivity, however, increases rapidly with the rise in temperature. At higher temperatures, it directly combines with some metals to form predominantly ionic nitrides and with non-metals, covalent nitrides. A few typical reactions are:



- iv) It combines with hydrogen at about 773 K in the presence of a catalyst (Haber's Process) to form ammonia:



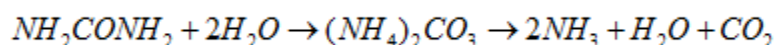
- v) Dinitrogen combines with dioxygen only at very high temperatures (at about 2000 K) to form nitric oxide, NO.

**Uses:**

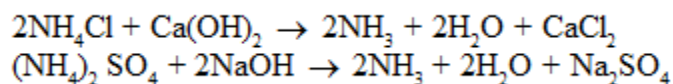
Liquid dinitrogen is used as a refrigerant to preserve biological materials, food items, and cryosurgery. The main use of dinitrogen is in the manufacture of ammonia and other industrial chemicals containing nitrogen, (e.g., calcium cyanamide).

### PREPARATION AMMONIA:

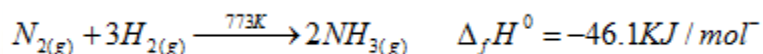
**Method-1:** Ammonia is present in small quantities in air and soil where it is formed by the decay of nitrogenous organic matter e.g., urea.



**Method-2:** On small scale ammonia is obtained from ammonium salts which decompose when treated with caustic soda or calcium hydroxide.



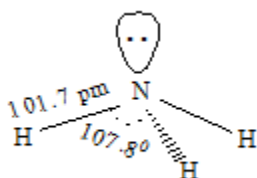
**Method-3:** On a large scale, ammonia is manufactured by Haber's process.



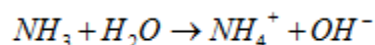
Following Le Chatelier's principle, high pressure would favor the formation of ammonia. The optimum conditions for the production of ammonia are a pressure of  $200 \times 10^5$  Pa (about 200 atm), a temperature of  $\sim 700$  K, and the use of a catalyst such as iron oxide with small amounts of  $K_2O$  and  $Al_2O_3$  to increase the rate of attainment of equilibrium.

### Properties:

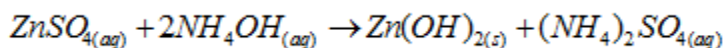
- Ammonia is a colorless gas with a pungent odor.
- Its freezing and boiling points are 198.4 and 239.7 K respectively.
- In the solid and liquid states, it is associated through hydrogen bonds as in the case of water and that accounts for its higher melting and boiling points than expected based on its molecular mass.
- The ammonia molecule is trigonal pyramidal with the nitrogen atom at the apex. It has three bond pairs and one lone pair of electrons.



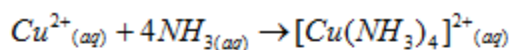
- Ammonia gas is highly soluble in water. Its aqueous solution is weakly basic due to the formation of  $OH^-$  ions.



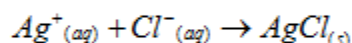
- f) It forms ammonium salts with acids, e.g.,  $\text{NH}_4\text{Cl}$ ,  $(\text{NH}_4)_2\text{SO}_4$ , etc. As a weak base, it precipitates the hydroxides (hydrated oxides in case of some metals) of many metals from their salt solutions. For example,



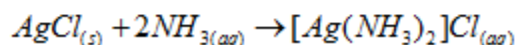
- g) The presence of a lone pair of electrons on the nitrogen atom of the ammonia molecule makes it a Lewis base. It donates the electron pair and forms linkage with metal ions and the formation of such complex compounds finds applications in detection of metal ions such as  $\text{Cu}^{2+}$ ,  $\text{Ag}^+$



(Blue) (deep blue)



(colourless) (White ppt)

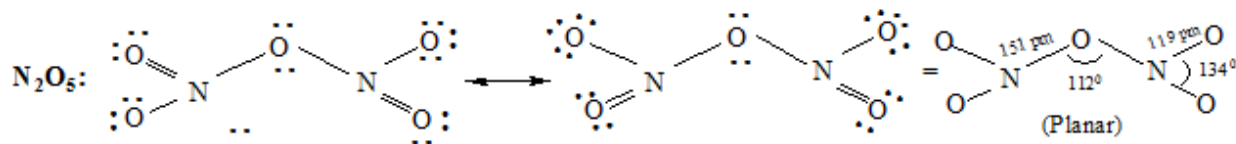
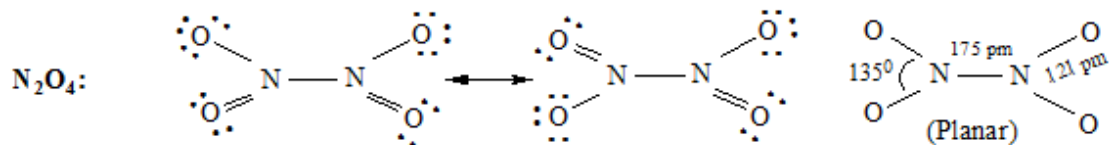
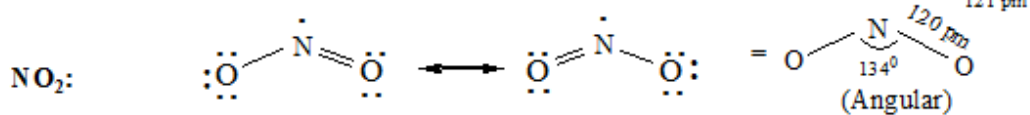
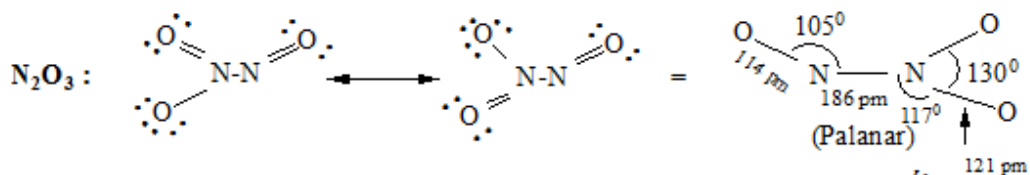
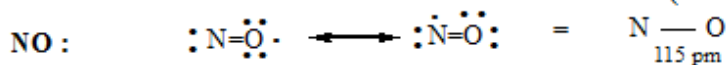
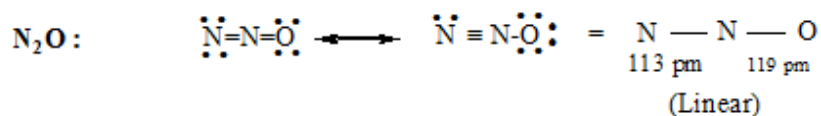


**Uses:** Ammonia is used to produce various nitrogenous fertilizers (ammonium nitrate, urea, ammonium phosphate, and ammonium sulfate) and in the manufacture of some inorganic nitrogen compounds, the most important one being nitric acid. Liquid ammonia is also used as a refrigerant.

### Oxides of Nitrogen:

| Name  | Formula                | O.S | Preparation  | Physical appearance and chemical nature |
|---|------------------------|-----|--|---|
| Dinitrogen Oxide<br>(Nitrogen(I)Oxide)      | $\text{N}_2\text{O}$   | +1  | $\text{NH}_4\text{NO}_3 \xrightarrow{\Delta} \text{N}_2\text{O} + 2\text{H}_2\text{O}$   | Colourless gas, neutral                 |
| Nitrogen monoxide<br>(Nitrogen(II)Oxide)    | $\text{NO}$            | +2  | $2\text{NaNO}_2 + 2\text{FeSO}_4 + 3\text{H}_2\text{SO}_4 \longrightarrow \text{Fe}_2(\text{SO}_4)_3 + 2\text{NaHSO}_4 + 2\text{H}_2\text{O} + 2\text{NO}$ | Colourless gas, neutral                 |
| Dinitrogen trioxide<br>(Nitrogen(III)Oxide) | $\text{N}_2\text{O}_3$ | +3  | $2\text{NO} + \text{N}_2\text{O}_4 \xrightarrow{250\text{K}} 2\text{N}_2\text{O}_3$  | Blue solid, acidic                      |
| Nitrogen dioxide<br>(Nitrogen(IV)Oxide)     | $\text{NO}_2$          | +4  | $2\text{Pb}(\text{NO}_3)_2 \xrightarrow{673\text{K}} 4\text{NO}_2 + 2\text{PbO}$   | Brown gas, acidic                       |
| Dinitrogen tetroxide<br>(Nitrogen(IV)Oxide) | $\text{N}_2\text{O}_4$ | +4  | $2\text{NO}_2 \xrightleftharpoons[\text{Heat}]{\text{Cool}} \text{N}_2\text{O}_4$  | Colourless solid / Liquid, acidic       |
| Dinitrogen pentoxide<br>(Nitrogen(V)Oxide)  | $\text{N}_2\text{O}_5$ | +5  | $4\text{HNO}_3 + \text{P}_4\text{O}_{10} \longrightarrow 4\text{HPO}_3 + 2\text{N}_2\text{O}_5$  | Colourless solid, acidic                |

## Structures of Oxides of Nitrogen:



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## LECTURE-3

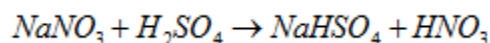
### PREPARATION OF NITRIC ACID (HNO<sub>3</sub>):

Nitrogen forms oxoacids such as H<sub>2</sub>N<sub>2</sub>O<sub>2</sub> (hyponitrous acid), HNO<sub>2</sub> (nitrous acid), and HNO<sub>3</sub> (nitric acid). HNO<sub>3</sub> is the most important among them.

#### Preparation:

##### **Method-1:**

In the laboratory, nitric acid is prepared by heating KNO<sub>3</sub> or NaNO<sub>3</sub> and concentrated H<sub>2</sub>SO<sub>4</sub> in a glass retort.

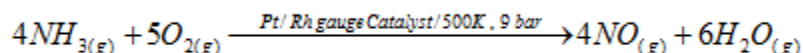


##### **Method-2:**

On a large scale, it is prepared mainly by Ostwald's process.

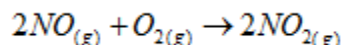
##### **Step-1:**

This method is based upon catalytic oxidation of NH<sub>3</sub> by atmospheric oxygen.



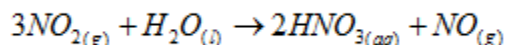
##### **Step-2:**

Nitric oxide thus formed combines with oxygen giving NO<sub>2</sub>.



##### **Step-3:**

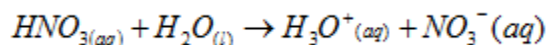
Nitrogen dioxide so formed, dissolves in water to give HNO<sub>3</sub>.



NO thus formed is recycled and the aqueous HNO<sub>3</sub> can be concentrated by distillation up to ~ 68% by mass. Further concentration to 98% can be achieved by dehydration with concentrated H<sub>2</sub>SO<sub>4</sub>.

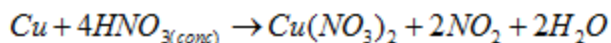
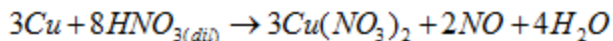
#### **Properties:**

- It is a colorless liquid (f.p. 231.4 K and b.p. 355.6 K).
- Laboratory grade nitric acid contains ~ 68% of the HNO<sub>3</sub> by mass and has a specific gravity of 1.504.
- In the gaseous state, HNO<sub>3</sub> exists as a planar molecule with the structure.
- In aqueous solution, nitric acid behaves as a strong acid giving hydronium and nitrate ions.

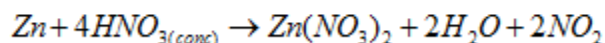
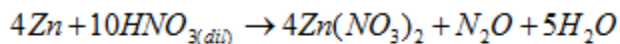


- Concentrated nitric acid is a strong oxidizing agent and attacks most metals except noble metals such as gold and platinum. The products of oxidation depend upon the concentration of the acid, temperature, and the nature of the material undergoing oxidation.

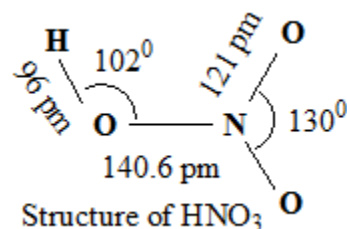
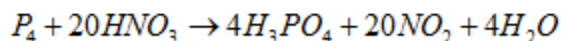
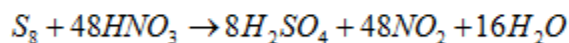
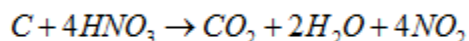
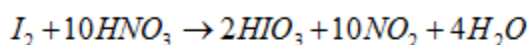




Zinc reacts with dilute nitric acid to give  $\text{N}_2\text{O}$  and with concentrated acid to give  $\text{NO}_2$ .

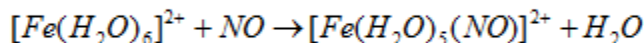
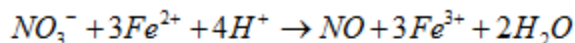


- (f) Some metals (e.g., Cr, Al) do not dissolve in concentrated nitric acid because of the formation of a passive film of oxide on the surface. Concentrated nitric acid also oxidizes non-metals and their compounds. Iodine is oxidized to iodic acid, carbon to carbon dioxide, sulfur to  $\text{H}_2\text{SO}_4$ , and phosphorus to phosphoric acid.



### Brown Ring Test:

- (i) The brown ring test for nitrates depends on the ability of  $\text{Fe}^{2+}$  to reduce nitrates to nitric oxide, which reacts with  $\text{Fe}^{2+}$  to form a brown colored complex.
- (ii) The test is usually done by adding dilute ferrous sulfate solution to an aqueous solution containing nitrate ion and then carefully adding concentrated sulphuric acid along the sides of the test tube. A brown ring at the interface between the solution and sulphuric acid layers indicates the presence of nitrate ion in solution.



*Brown ring*

### Uses:

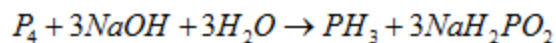
- It is used in the manufacture of ammonium nitrate for fertilizers and other nitrates for use in explosives and pyrotechnics.
- It is also used for the preparation of nitroglycerin, trinitrotoluene, and other organic nitro compounds.
- Other major uses are in the *pickling of stainless steel*, etching of metals, and as an oxidizer in rocket fuels.

### ALLOTROPIC FORMS OF PHOSPHORUS

The important allotropic forms of phosphorus are white, red, and black.

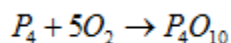
#### White phosphorus:

- It is a translucent white waxy solid. It is poisonous, insoluble in water but soluble in carbon disulfide and glows in dark (chemiluminescence).
- It dissolves in boiling  $\text{NaOH}$  solution in an inert atmosphere giving  $\text{PH}_3$ .

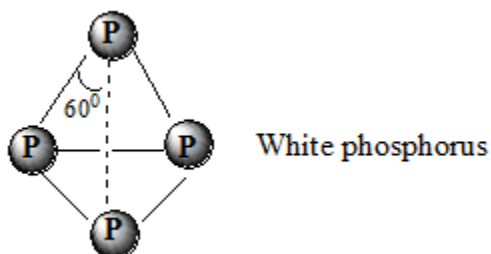


Sodium hypophosphite

- (iii) White phosphorus is less stable and therefore, more reactive than the other solid phases under normal conditions because of angular strain in the  $P_4$  molecule where the angles are only  $60^\circ$ .
- (iv) It readily catches fire in the air to give dense white fumes of  $P_4O_{10}$ .

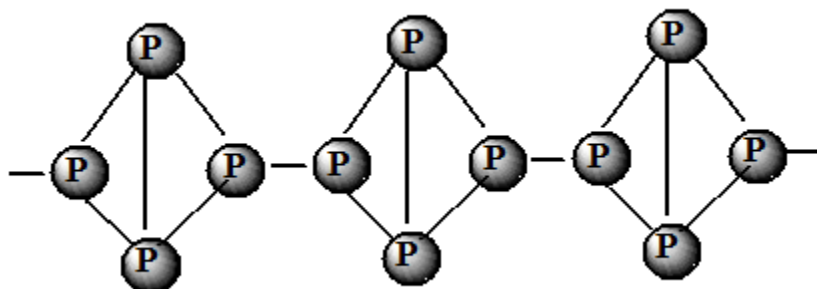


- (v)  $P_4$  molecule is tetrahedral.



### Red phosphorus:

- (i) It is obtained by heating white phosphorus at 573K in an inert atmosphere for several days.
- (ii) When red phosphorus is heated under high pressure, a series of phases of black phosphorus is formed.
- (iii) Red phosphorus possesses an iron-grey luster. It is odorless, nonpoisonous, and insoluble in water as well as in carbon disulfide.
- (iv) Chemically, red phosphorus is much less reactive than white phosphorus. It does not glow in the dark. It has a polymeric chain structure.

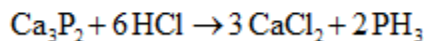
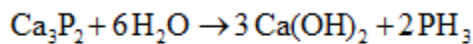


### Black phosphorus:

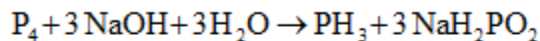
- (i) It has two forms alpha -black phosphorus and beta -black phosphorus.
- (ii) **Alfa-Black phosphorus** is formed when red phosphorus is heated in a sealed tube at 803K. It can be sublimed in air and has opaque monoclinic or rhombohedral crystals. It does not oxidize in air.
- (iii) **Beta-Black phosphorus** is prepared by heating white phosphorus at 473 K under high pressure. It does not burn in the air up to 673 K.

**Preparation of Phosphine:****Method-1:**

Phosphine is prepared by the reaction of calcium phosphide with water or dilute HCl.

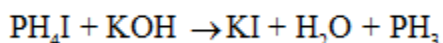
**Method-2:**

In the laboratory, it is prepared by heating white phosphorus with concentrated NaOH solution in an inert atmosphere of  $\text{CO}_2$ .

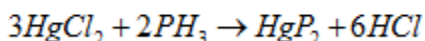
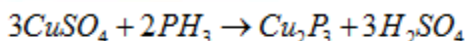


Sod. hypophosphite

When pure, it is non-inflammable but becomes inflammable owing to the presence of  $\text{P}_2\text{H}_4$  or  $\text{P}_4$  vapors. It is absorbed in HI to form phosphonium iodide ( $\text{PH}_4\text{I}$ ) which on treating with KOH gives off phosphine.

**Properties:**

- It is a colorless gas with a rotten fish smell and is highly poisonous.
- It explodes in contact with traces of oxidizing agents like  $\text{HNO}_3$ ,  $\text{Cl}_2$ , and  $\text{Br}_2$  vapors.
- It is slightly soluble in water. The solution of  $\text{PH}_3$  in water decomposes in presence of light giving red phosphorus and  $\text{H}_2$ . When absorbed in copper sulfate or mercuric chloride solution, the corresponding phosphides are obtained.



- Phosphine is weakly basic and like ammonia, gives phosphonium compounds with acids.  
e.g.,  $\text{PH}_3 + \text{HBr} \rightarrow \text{PH}_4\text{Br}$

**Uses:**

- The spontaneous combustion of phosphine is technically used in *Holme's signals*.
- Containers containing calcium carbide and calcium phosphide are pierced and thrown in the sea when the gases evolved to burn and serve as a signal. It is also used in *smoke screens*.

**Answer the following questions:**

- In what way can it be proved that  $\text{PH}_3$  is basic?
- The bond angle in  $\text{PH}_4^+$  is higher than that in  $\text{PH}_3$ . Why?
- What happens when white phosphorus is heated with conc. NaOH solution in an inert atmosphere of  $\text{CO}_2$ ?
- Write the main differences between the properties of white phosphorus and red phosphorus.
- Give the disproportionation reaction of  $\text{H}_3\text{PO}_3$ .

6. How will you prepare nitric acid in the laboratory?
7. Discuss the different steps to prepare nitric acid in Ostwald's process.
8. Name the catalysts used in Ostwald's process.
9. How do Zn and Copper react with concentrated and dilute nitric acid? Write equations.
10. How does conc? Does nitric acid react with non-metals? Give equations.
11. Illustrate how copper metal can give different products on reaction with  $\text{HNO}_3$ .

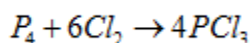
## LECTURE-4

### HALIDES OF PHOSPHORUS:

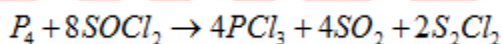
#### a) Phosphorus Trichloride:

##### Preparation:

- (i) It is obtained by passing dry chlorine over heated white phosphorus.

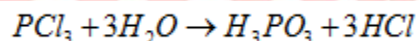


- (ii) It is also obtained by the action of thionyl chloride with white phosphorus.

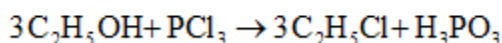
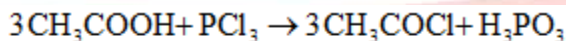


##### Properties:

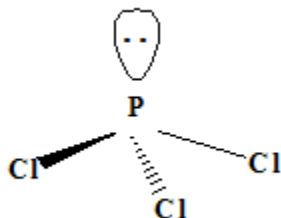
- a) It is a colorless oily liquid and hydrolyses in the presence of moisture.



- b) It reacts with organic compounds containing -OH group such as  $\text{CH}_3\text{COOH}$ ,  $\text{C}_2\text{H}_5\text{OH}$ .



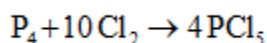
It has a pyramidal shape as shown, in which phosphorus is  $sp^3$  hybridized.



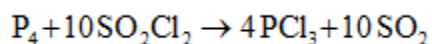
#### Phosphorus pentachloride:

##### Preparation:

- (i) Phosphorus pentachloride is prepared by the reaction of white phosphorus with an excess of dry chlorine.

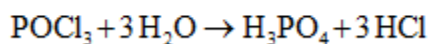
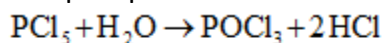


- (ii) It can also be prepared by the action of  $\text{SO}_2\text{Cl}_2$  on phosphorus.

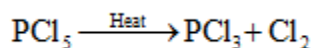


##### Properties:

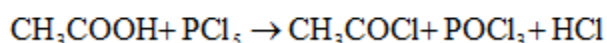
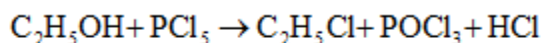
a)  $\text{PCl}_5$  is a yellowish-white powder and in moist air, it hydrolyses to  $\text{POCl}_3$  and finally gets converted to phosphoric acid.



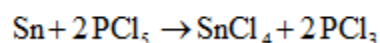
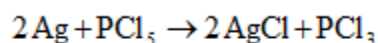
b) On heating, it sublimes but decomposes on stronger heating.



c) It reacts with organic compounds containing  $-\text{OH}$  group converting them to chloro derivatives.

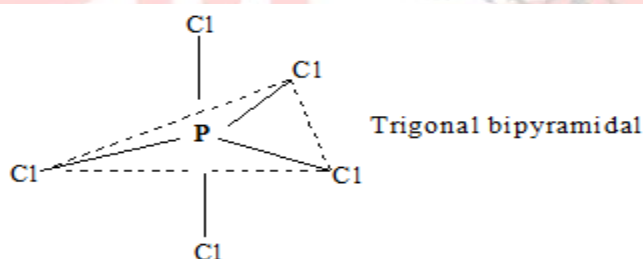


d) Finely divided metals on heating with  $\text{PCl}_5$  give corresponding chlorides.



e) It is used in the synthesis of some organic compounds, e.g.,  $\text{C}_2\text{H}_5\text{Cl}$ ,  $\text{CH}_3\text{COCl}$ .

f) In gaseous and liquid phases, it has a trigonal bipyramidal structure. The three equatorial  $\text{P}-\text{Cl}$  bonds are equivalent, while the two axial bonds are longer than equatorial bonds. This is because the axial bond pairs suffer more repulsion as compared to equatorial bond pairs.



g) In the solid-state, it exists as an ionic solid,  $[\text{PCl}_4]^+[\text{PCl}_6]^-$  in which the cation,  $[\text{PCl}_4]^+$  is tetrahedral and the anion,  $[\text{PCl}_6]^-$  octahedral.

### OXOACIDS OF PHOSPHORUS:

(i) **Hypophosphorous / Phosphinic** ( $\text{H}_3\text{PO}_2$ ), [O.N= +1, One  $\text{P}-\text{OH}$ , two  $\text{P}-\text{H}$  and one  $\text{P}=\text{O}$ , Preparation:  $\text{P}_4 + \text{Alkali}$ ].

(ii) **Orthophosphorous / Phosphinic** ( $\text{H}_3\text{PO}_3$ ), [O.N= +3, Two  $\text{P}-\text{OH}$ , One  $\text{P}-\text{H}$  and  $\text{P}=\text{O}$ , Preparation:  $\text{P}_2\text{O}_3 + \text{H}_2\text{O}$ ].

(iii) **Pyrophosphorous** ( $\text{H}_4\text{P}_2\text{O}_5$ ), [O.N= +3, Two  $\text{P}-\text{OH}$ , Two  $\text{P}-\text{H}$ , Two  $\text{P}=\text{O}$ , Preparation:  $\text{PCl}_3 + \text{H}_3\text{PO}_3$ ]

(iv) **Hypophosphoric** ( $\text{H}_4\text{P}_2\text{O}_6$ ), [O.N= +4, Four  $\text{P}-\text{OH}$ , Two  $\text{P}=\text{O}$ , One  $\text{P}-\text{P}$ , Preparation: Red P + Alkali.]

(v) **Orthophosphoric** ( $\text{H}_3\text{PO}_4$ ), [O.N= +5, Three  $\text{P}-\text{OH}$ , One  $\text{P}=\text{O}$ , Preparation:  $\text{P}_4\text{O}_{10} + \text{H}_2\text{O}$ ]

(vi) **Pyrophosphoric ( $H_4P_2O_7$ )**, [O.N= +5, Four P-OH, Two P=O, One P-O-P]

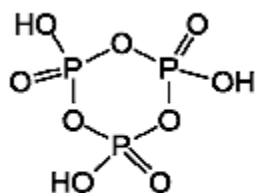
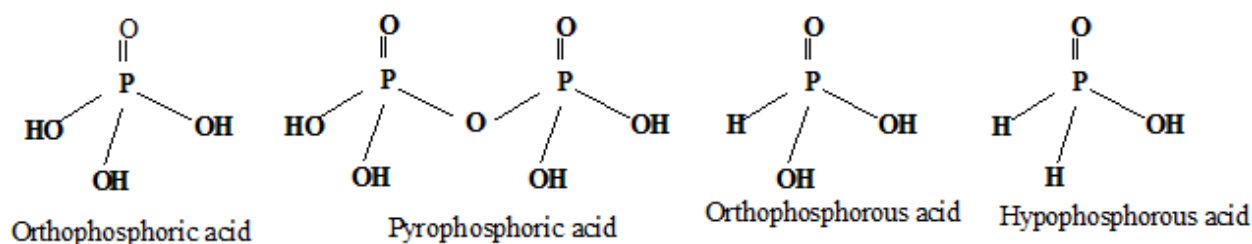
**Preparation:** By heating Phosphoric acid].

(vii) **Metaphosphoric ( $(HPO_3)_n$** , [O.N= +5, Three P-OH, Three P=O, Three P-O-P,

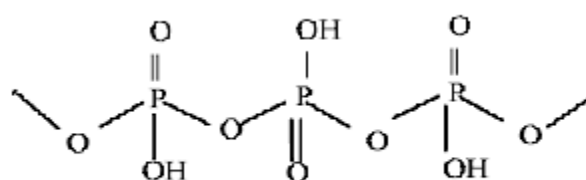
**Preparation:** Heating of Phosphorus acid +  $Br_2$  in a sealed tube].

The composition of oxoacid is interrelated in terms of loss or gain of  $H_2O$  or O-atom.

### Structure:



Cyclotrimetaphosphoric acid ( $(HPO_3)_3$ )



Polymetaphosphoric acid ( $(HPO_3)_n$ )

- (i) In oxoacids, phosphorus is tetrahedrally surrounded by other atoms.
- (ii) All these acids contain at least one P=O bond and one P-OH bond.
- (iii) The oxoacids in which phosphorus has a lower oxidation state (less than +5) contain, in addition to P=O and P-OH bonds, either P-P (e.g., in  $H_4P_2O_6$ ) or P-H (e.g., in  $H_3PO_2$ ) bonds but not both.
- (iv) These acids in the +3 oxidation state of phosphorus tend to disproportionate to higher and lower oxidation states. For example, orthophosphorous acid (or phosphorous acid) on heating disproportionates to give orthophosphoric acid (or phosphoric acid) and phosphine.
- (v) The acids which contain P-H bond have strong reducing properties. Thus, hypophosphorous acid is a good reducing agent as it contains two P-H bonds and reduces.  
for example,  $AgNO_3$  to metallic silver.

- (vi) These P–H bonds are not ionizable to give  $H^+$  and do not play any role in basicity. Only those H atoms which are attached with oxygen in P–OH form are ionizable and cause the basicity.
- (vii) Thus,  $H_3PO_3$  and  $H_3PO_4$  are dibasic and tribasic, respectively as the structure of  $H_3PO_3$  has two P–OH bonds and  $H_3PO_4$  three.

## LECTURE-5

### GROUP-16 (OXYGEN FAMILY)

Oxygen, sulfur, selenium, tellurium, and polonium constitute Group 16 of the periodic table. This is also known as **chalcogens**.

#### Occurrence:

- (i) Oxygen is the most abundant of all the elements on earth. Oxygen forms about 46.6% by mass of earth's crust. Dry air contains 20.946% oxygen by volume.
- (ii) The abundance of sulfur in the earth's crust is only 0.03-0.1%.
- (iii) Combined sulfur exists primarily as sulfates such as **gypsum**  $CaSO_4 \cdot 2H_2O$ , **Epsom salt**  $MgSO_4 \cdot 7H_2O$ , **baryte**  $BaSO_4$  and sulfides such as **galena**  $PbS$ , **zinc blende**  $ZnS$ , **copper pyrites**  $CuFeS_2$ .
- (iv) Traces of sulfur occur as hydrogen sulfide in volcanoes.
- (v) Organic materials such as eggs, proteins, garlic, onion, mustard, hair, and wool contain sulfur.
- (vi) Selenium and tellurium are also found as metal selenides and tellurides in sulfide ores.
- (vii) 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  $ns^2np^4$  general electronic configuration.

#### Atomic and Ionic Radii:

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

#### Ionization enthalpy:

It decreases down the group. It is due to an increase in size. However, the elements of this group have lower ionization enthalpy values compared to those of Group 15 in the corresponding periods. This is because Group 15 elements have extra stable half-filled  $p$ -orbitals electronic configurations.

#### Electron Gain Enthalpy:

Because of the compact nature of the oxygen atom, it has less negative electron gain enthalpy than sulfur. However, from sulfur onwards, the value again becomes less negative up to polonium.

#### Electronegativity:

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

#### **Physical Properties:**

- (i) Oxygen and sulfur are non-metals, selenium, and tellurium metalloids, whereas polonium is a metal. Polonium is radioactive and is short-lived (Half-life 13.8 days).
- (ii) All these elements exhibit allotropy.
- (iii) The melting and boiling points increase with an increase in the atomic number down the group.
- (iv) The large difference between the melting and boiling points of oxygen and sulfur may be explained based on their atomicity; oxygen exists as a diatomic molecule ( $O_2$ ) whereas sulfur exists as a polyatomic molecule ( $S_8$ ).

#### **Chemical Properties:**

##### **Oxidation states and trends in chemical reactivity:**

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

##### **Anomalous behavior of oxygen:**

- i) The anomalous behavior of oxygen is due to its small size and high electronegativity.
- ii) Due to small size and high electronegativity, it forms strong hydrogen bonding in  $H_2O$  which is not found in  $H_2S$ .
- iii) The absence of  $d$  orbitals in oxygen limits its covalency to four and in practice, rarely exceeds two.
- iv) On the other hand, in the case of other elements of the group, the valence shells can be expanded and covalence exceeds four.

##### **Reactivity with hydrogen:**

- a)** All the elements of Group 16 form hydrides of the type  $H_2E$  ( $E = O, S, Se, Te, Po$ ). Their acidic character increases from  $H_2O$  to  $H_2Te$ . The increase in acidic character can be explained in terms of a decrease in bond enthalpy for the dissociation of H-E bond down the group.
- b)** Owing to the decrease in enthalpy for the dissociation of H-E bond down the group, the thermal stability of hydrides also decreases from  $H_2O$  to  $H_2Po$ .
- c)** All the hydrides except water possess the reducing property and this character increases from  $H_2S$  to  $H_2Te$ .



vi) **Reactivity with oxygen:**

a) All these elements form oxides of the  $EO_2$  and  $EO_3$  types where E = S, Se, Te, or Po.

Ozone ( $O_3$ ) and sulfur dioxide ( $SO_2$ ) are gases while selenium dioxide ( $SeO_2$ ) is solid.

b) Reducing the property of dioxide decreases from  $SO_2$  to  $TeO_2$ ;  $SO_2$  is reducing while  $TeO_2$  is an oxidizing agent.

c) Besides  $EO_2$  type, sulfur, selenium, and tellurium also form  $EO_3$  type oxides ( $SO_3$ ,  $SeO_3$ ,  $TeO_3$ ). Both types of oxides are acidic.

vii) **Reactivity towards the halogens:**

a) Elements of Group 16 form a large number of halides of the type,  $EX_6$ ,  $EX_4$ , and  $EX_2$  where E is an element of the group, and X is a halogen.

b) The stability of the halides decreases in the order  $F^- > Cl^- > Br^- > I^-$ .

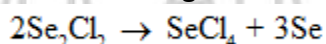
c) Amongst hexahalides, hexafluorides are the only stable halides. All hexafluorides are gaseous. They have an octahedral structure. Sulphur hexafluoride,  $SF_6$  is exceptionally stable for steric reasons.

d) Amongst tetrafluorides,  $SF_4$  is a gas,  $SeF_4$  a liquid, and  $TeF_4$  a solid.

e) These fluorides have  $sp^3d$  hybridization and thus, have trigonal bipyramidal structures in which one of the equatorial positions is occupied by a lone pair of electrons. This geometry is also regarded as **see-saw** geometry.

f) All elements except oxygen form dichlorides and dibromides. These dihalides are formed by  $sp^3$  hybridization and thus, have a tetrahedral structure. The well-known monohalides are dimeric.

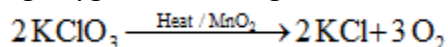
**Examples:**  $S_2F_2$ ,  $S_2Cl_2$ ,  $S_2Br_2$ ,  $Se_2Cl_2$  and  $Se_2Br_2$ . These dimeric halides undergo disproportionation as given below:



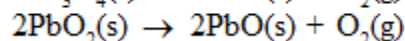
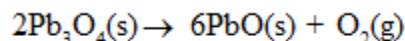
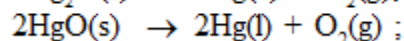
## LECTURE-6

**PREPARATION OF DIOXYGEN:****Method-1:**

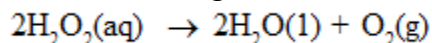
By heating oxygen-containing salts such as chlorates, nitrates, and permanganates.

**Method-2:**

By the thermal decomposition of the oxides of metals low in the electrochemical series and higher oxides of some metals.

**Method-3:**

Hydrogen peroxide is readily decomposed into water and dioxygen by catalysts such as finely divided metals and manganese dioxide.



**Method-4:**

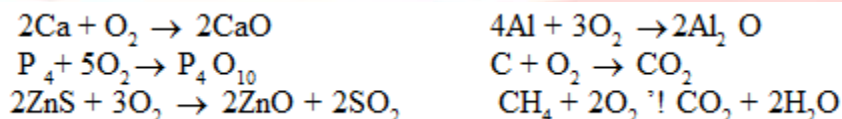
On a large scale, it can be prepared from water or air. The electrolysis of water leads to the release of hydrogen at the cathode and oxygen at the anode.

**Method-5:**

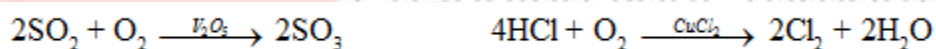
Industrially, dioxygen is obtained from air by first removing carbon dioxide and water vapor, and then, the remaining gases are liquefied and fractionally distilled to give dinitrogen and dioxygen.

**Properties:**

- (i) Dioxygen is a colorless and odorless gas.
- (ii) Its solubility in water is to the extent of 3.08 cm<sup>3</sup> in 100 cm<sup>3</sup> water at 293 K which is just sufficient for the vital support of marine and aquatic life. It liquefies at 90 K and freezes at 55 K.
- (iii) The oxygen atom has three stable isotopes: <sup>16</sup>O, <sup>17</sup>O, and <sup>18</sup>O. Molecular oxygen, O<sub>2</sub> is unique in being paramagnetic despite having an even number of electrons.
- (iv) Dioxygen directly reacts with nearly all metals and non-metals except some metals (e.g., Au, Pt) and some noble gases.
- (v) Its combination with other elements is often strongly exothermic which helps in sustaining the reaction. However, to initiate the reaction, some external heating is required as bond dissociation enthalpy of the oxygen-oxygen double bond is high (493.4 kJ mol<sup>-1</sup>).
- (vi) Some of the reactions of dioxygen with metals, non-metals, and other compounds are given below:



- (vii) Some compounds are catalytically oxidized. For example,

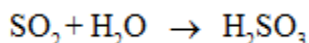
**Uses:**

- (i) It is in normal respiration and combustion processes.
- (ii) Oxygen is used in oxyacetylene welding, in the manufacture of many metals, particularly steel.
- (iii) Oxygen cylinders are widely used in hospitals, high altitude flying, and mountaineering.
- (iv) The combustion of fuels, e.g., hydrazines in liquid oxygen, provides tremendous thrust in rockets.

**Simple Oxides:**

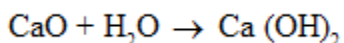
- a) A binary compound of oxygen with another element is called oxide. Oxygen reacts with most of the elements of the periodic table to form oxides. In many cases, one element forms two or more oxides.
- b) Oxides can be simple (e.g., MgO, Al<sub>2</sub>O<sub>3</sub>) or mixed (Pb<sub>3</sub>O<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub>). Simple oxides can be classified based on their acidic, basic or amphoteric character.

- c) An oxide that combines with water to give an acid is termed acidic oxide (e.g.,  $\text{SO}_2$ ,  $\text{Cl}_2\text{O}_7$ ,  $\text{CO}_2$ ,  $\text{N}_2\text{O}_5$ ). For example,  $\text{SO}_2$  combines with water to give  $\text{H}_2\text{SO}_3$ .

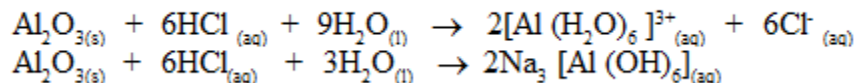


- d) Only non-metal oxides are acidic but oxides of some metals in high oxidation state also have acidic character (e.g.,  $\text{Mn}_2\text{O}_7$ ,  $\text{CrO}_3$ ,  $\text{V}_2\text{O}_5$ ).

- e) The oxides which give a base with water are known as basic oxides (e.g.,  $\text{Na}_2\text{O}$ ,  $\text{CaO}$ , and  $\text{BaO}$ ). For example,  $\text{CaO}$  combines with water to give  $\text{Ca}(\text{OH})_2$ .



- f) Metallic oxides are basic. Some metallic oxides exhibit a dual behavior. They show characteristics of both acidic as well as basic oxides. Such oxides are known as amphoteric oxides. They react with acids as well as alkalies. For example,  $\text{Al}_2\text{O}_3$  reacts with acids as well as alkalies.



Some oxides are neither acidic nor basic. Such oxides are known as neutral oxides. Ex:  $\text{CO}$ ,  $\text{NO}$ ,  $\text{N}_2\text{O}$ .

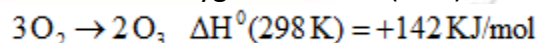
## LECTURE-7

### OZONE ( $\text{O}_3$ )

Ozone is an allotropic form of Oxygen. It is present at sea level. At a high altitude of about 20 km, it is formed by the action of ultraviolet light on atmospheric oxygen.

#### Preparation:

When a slow dry stream of oxygen is passed through a silent electrical discharge, conversion of oxygen to ozone (10%) occurs. The product is known as ozonized oxygen.



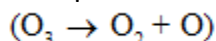
Since the formation of ozone from oxygen is an endothermic process, it is necessary to use a silent electrical discharge in its preparation to prevent its decomposition.

If concentrations of ozone greater than 10 percent are required, a battery of ozonizers can be used and pure ozone (b.p. 101.1K) can be condensed in a vessel surrounded by liquid oxygen.

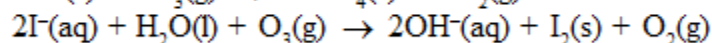
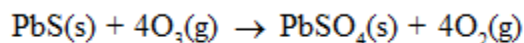
#### Properties:

- (i) Pure ozone is a pale blue gas, dark blue liquid, and violet-black solid.
- (ii) Ozone has a characteristic smell and in small concentrations it is harmless.
- (iii) However, if the concentration rises above about 100 parts per million, breathing becomes uncomfortable resulting in headache and nausea.
- (iv) Ozone is thermodynamically unstable concerning oxygen since its decomposition into oxygen results in the liberation of heat ( $\Delta H$  is negative) and an increase in entropy ( $\Delta S$  is positive).
- (v) These two effects reinforce each other, resulting in large negative Gibbs energy change ( $\Delta G$ ) for its conversion into oxygen.

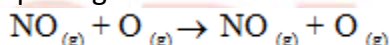
- (vi) therefore, high concentrations of ozone can be dangerously explosive.  
 (vii) It is a powerful oxidizing agent. Because it liberates nascent oxygen.



**For example-** Oxidises lead sulfide to lead sulfate and iodide ions to iodine.



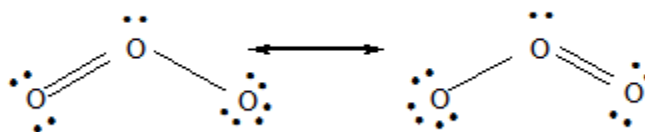
- (viii) **Estimation of Ozone:** When ozone reacts with an excess of potassium iodide solution buffered with a borate buffer (pH = 9.2), iodine is liberated which can be titrated against a standard solution of sodium thiosulphate. This is a quantitative method for estimating O<sub>3</sub> gas.
- (ix) **Depletion of Ozone:** Experiments have shown that nitrogen oxides (particularly nitric oxide) combine very rapidly with ozone and there is, thus, the possibility that nitrogen oxides emitted from the exhaust systems of supersonic jet airplanes might be slowly depleting the concentration of the ozone layer in the upper atmosphere.



Another threat to this ozone layer is probably posed by the use of freons which are used in aerosol sprays and as refrigerants.

### Structure of Ozone:

The two oxygen-oxygen bond lengths in the ozone molecule are identical (128 pm) and the molecule is angular as expected with a bond angle of about 117°. It is a resonance hybrid of two main forms:



**Uses:** It is used as a germicide, disinfectant, and sterilizing water. It is also used for bleaching oils, ivory, flour, starch, etc. It acts as an oxidizing agent in the manufacture of potassium permanganate.

### **ALLOTROPIC FORMS SULPHUR:**

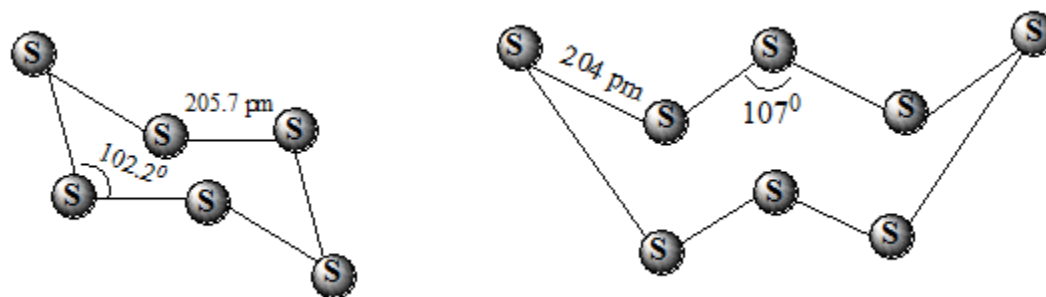
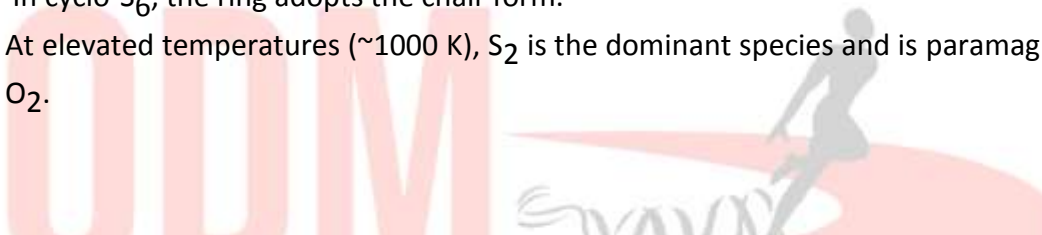
Yellow rhombic (alpha-sulfur) and monoclinic (beta-sulfur) forms are the most important allotropic forms. The stable form at room temperature is rhombic sulfur, which transforms into monoclinic sulfur when heated above 369 K.

#### Rhombic sulfur (alpha-sulfur):

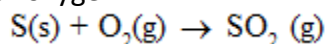
- (i) This allotrope is yellow, m.p. 385.8 K, and specific gravity 2.06.
- (ii) Rhombic sulfur crystals are formed on evaporating the solution of roll sulfur in CS<sub>2</sub>.
- (iii) It is insoluble in water but dissolves to some extent in benzene, alcohol, and ether. It is readily soluble in CS<sub>2</sub>.

**Monoclinic sulfur (beta-sulfur):**

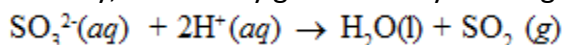
- (i) Its m.p. is 393 K and specific gravity 1.98.
- (ii) It is soluble in CS<sub>2</sub>.
- (iii) This form of sulfur is prepared by melting rhombic sulfur in a dish and cooling, till crust is formed. Two holes are made in the crust and the remaining liquid poured out. On removing the crust, colorless needle-shaped crystals of beta-sulfur are formed.
- (iv) It is stable above 369 K and transforms into alfa-sulfur below it. Conversely, alfa-sulfur is stable below 369 K and transforms into beta-sulfur above this.
- (v) At 369 K both the forms are stable. This temperature is called transition temperature.
- (vi) Both rhombic and monoclinic sulfur have S<sub>8</sub> molecules.
- (vii) These S<sub>8</sub> molecules are packed to give different crystal structures. The S<sub>8</sub> ring in both forms is puckered and has a crown shape.
- (viii) Several other modifications of sulfur-containing 6-20 sulfur atoms per ring have been synthesized in the last two decades.
- (ix) In cyclo-S<sub>6</sub>, the ring adopts the chair form.
- (x) At elevated temperatures (~1000 K), S<sub>2</sub> is the dominant species and is paramagnetic like O<sub>2</sub>.

**SULPHUR DIOXIDE:****Preparation:****Method-1:**

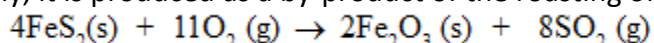
Sulphur dioxide is formed together with a little (6-8%) sulfur trioxide when sulfur is burnt in air or oxygen:

**Method-2:**

In the laboratory, it is readily generated by treating a sulfite with dilute sulphuric acid.

**Method-3:**

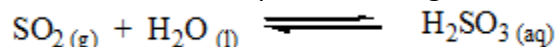
Industrially, it is produced as a by-product of the roasting of sulfide ores.



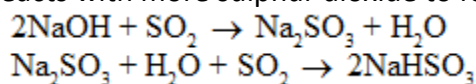
The gas after drying is liquefied under pressure and stored in steel cylinders.

**Properties:**

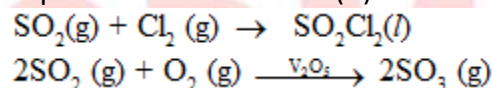
- (i) Sulphur dioxide is a colorless gas with a pungent smell and is highly soluble in water.  
 (ii) It liquefies at room temperature under a pressure of two atmospheres and boils at 263 K.  
 (iii) Sulphur dioxide, when passed through water, forms a solution of sulphurous acid.



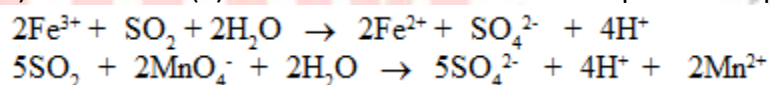
- (iv) It reacts readily with sodium hydroxide solution, forming sodium sulphite, which then reacts with more sulphur dioxide to form sodium hydrogen sulphite.



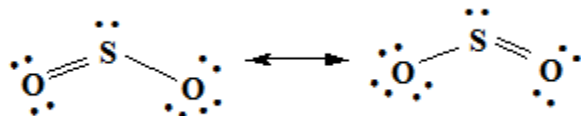
- (v) In its reaction with water and alkalis, the behavior of sulphur dioxide is very similar to that of carbon dioxide.  
 (vi) Sulphur dioxide reacts with chlorine in the presence of charcoal (which acts as a catalyst) to give sulphuryl chloride,  $\text{SO}_2\text{Cl}_2$ . It is oxidized to sulphur trioxide by oxygen in the presence of vanadium (V) oxide catalyst.



- (vii) When moist, sulphur dioxide behaves as a reducing agent. For example, it converts iron (III) ions to iron (II) ions and decolorizes acidified potassium permanganate (VII) solution.

**Structure of  $\text{SO}_2$ :**

The molecule of  $\text{SO}_2$  is angular. It is a resonance hybrid of the two canonical forms:



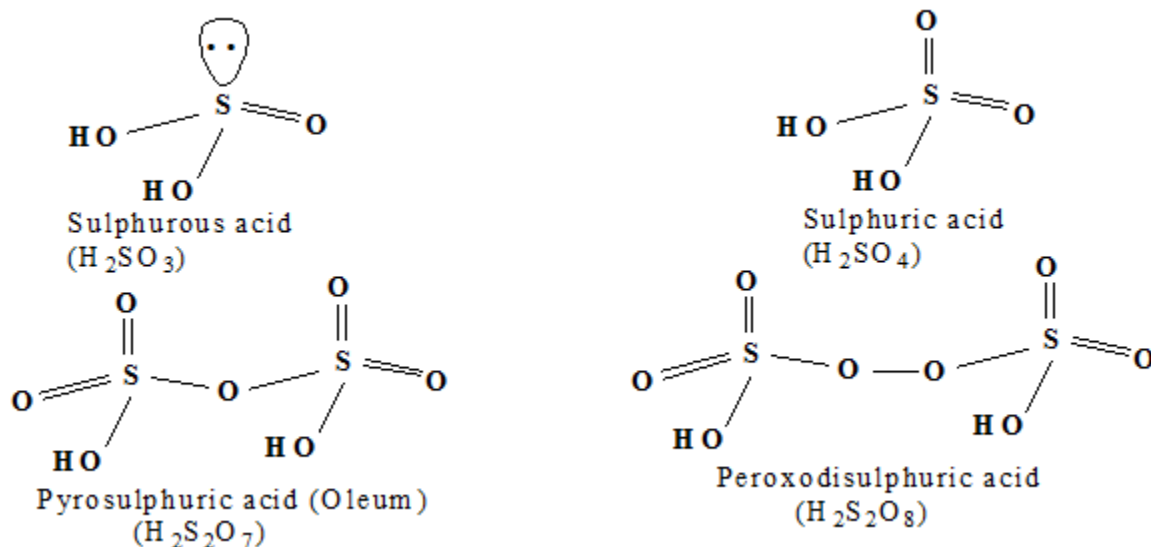
L GROUP  
 our Tomorrow

**Uses:**

- (i) Sulphur dioxide is used in refining petroleum and sugar.  
 (ii) It is used in bleaching wool and silk.  
 (iii) It is used as an antichlor, disinfectant, and preservative.  
 (iv) It is used in the manufacture of Sulphuric acid, sod. Hydrogen sulphite and calcium hydrogen sulphite.  
 (v) Liquid  $\text{SO}_2$  is used as a solvent to dissolve several organic and inorganic chemicals. acid, sodium hydrogen sulphite, and calcium hydrogen sulphite (industrial chemicals) are manufactured from sulphur dioxide. Liquid  $\text{SO}_2$  is used as a solvent to dissolve several organic and inorganic chemicals.

**Oxoacids of Sulphur:**

Sulphur forms several oxoacids such as  $\text{H}_2\text{SO}_3$ ,  $\text{H}_2\text{S}_2\text{O}_3$ ,  $\text{H}_2\text{S}_2\text{O}_4$ ,  $\text{H}_2\text{S}_2\text{O}_5$ ,  $\text{H}_2\text{S}_x\text{O}_6$  ( $x = 2$  to  $5$ ),  $\text{H}_2\text{SO}_4$ ,  $\text{H}_2\text{S}_2\text{O}_7$ ,  $\text{H}_2\text{SO}_5$ ,  $\text{H}_2\text{S}_2\text{O}_8$ . Some of these acids are unstable and cannot be isolated. They are known in aqueous solutions or the form of their salts.

**SULPHURIC ACID****Manufacture:**

Sulphuric acid is manufactured by the Contact Process which involves three steps:

**Step-1:**

Burning of sulphur or sulphide ores in the air to generate  $\text{SO}_2$ .

**Step-2:**

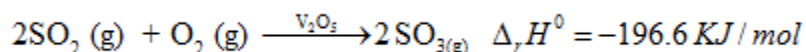
Conversion of  $\text{SO}_2$  to  $\text{SO}_3$  by the reaction with oxygen in the presence of a catalyst ( $\text{V}_2\text{O}_5$ ).

**Step-3:**

Absorption of  $\text{SO}_3$  in  $\text{H}_2\text{SO}_4$  to give Oleum ( $\text{H}_2\text{S}_2\text{O}_7$ ).

**Description:**

- The  $\text{SO}_2$  produced is purified by removing dust and other impurities such as arsenic compounds.
- The important step in the manufacture of  $\text{H}_2\text{SO}_4$  is the catalytic oxidation of  $\text{SO}_2$  with  $\text{O}_2$  to give  $\text{SO}_3$  in the presence of  $\text{V}_2\text{O}_5$  (catalyst).



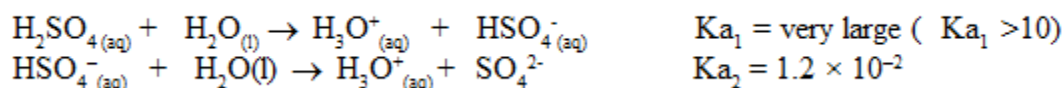
- The reaction is exothermic, reversible and the forward reaction leads to a decrease in volume. Therefore, low temperature and high pressure are favorable conditions for maximum yield. But the temperature should not be very low otherwise the rate of reaction will become slow.

- iv) The process is operated at a pressure of 2 bars and a temperature of 720 K.
- (v) The  $\text{SO}_3$  gas from the catalytic converter is absorbed in concentrated  $\text{H}_2\text{SO}_4$  to produce oleum.  

$$\text{SO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{H}_2\text{S}_2\text{O}_7 \text{ (Oleum)}$$
- (vi) Dilution of oleum with water gives  $\text{H}_2\text{SO}_4$  of the desired concentration. The sulphuric acid obtained by the Contact process is 96-98% pure.

**Properties:**

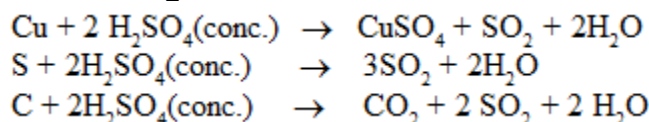
- (i) Sulphuric acid is a colorless, dense, oily liquid with a specific gravity of 1.84 at 298 K.
- (ii) The acid freezes at 283 K and boils at 611 K.
- (iii) It dissolves in water with the evolution of a large quantity of heat. Hence, care must be taken while preparing a sulphuric acid solution from concentrated sulphuric acid. The concentrated acid must be added slowly into the water with constant stirring.
- (iv) The chemical reactions of sulphuric acid are as a result of the following characteristics:  
 (a) Low volatility (b) strong acidic character  
 (c) Strong affinity for water and (d) ability to act as an oxidizing agent.
- (v) In aqueous solution, sulphuric acid ionises in two steps.



- (vi) The larger value of  $K_{a_1}$  ( $K_{a_1} > 10$ ) means that  $\text{H}_2\text{SO}_4$  is largely dissociated into  $\text{H}^+$  and  $\text{HSO}_4^-$ .
- (vii) Greater the value of the dissociation constant ( $K_a$ ), the stronger is the acid. The acid forms two series of salts: normal sulphates (such as sodium sulphate and copper sulphate) and acid sulphates (e.g., sodium hydrogen sulphate).
- (viii) Sulphuric acid, because of its low volatility can be used to manufacture more volatile acids from their corresponding salts.  

$$2 \text{MX} + \text{H}_2\text{SO}_4 \rightarrow 2 \text{HX} + \text{M}_2\text{SO}_4 (\text{X} = \text{F, Cl, NO}_3) \quad (\text{M} = \text{Metal})$$
- (ix) Concentrated sulphuric acid is a strong dehydrating agent.
- (x) Many wet gases can be dried by passing them through sulphuric acid, provided the gases do not react with the acid.
- (xi) Sulphuric acid removes water from organic compounds; it is evident by its charring action on carbohydrates.  

$$\text{C}_{12}\text{H}_{22}\text{O}_{11} \xrightarrow{\text{H}_2\text{SO}_4} 12\text{C} + 11\text{H}_2\text{O}$$
- (xii) Hot concentrated sulphuric acid is a moderately strong oxidizing agent. In this respect, it is intermediate between phosphoric and nitric acids.
- (xiii) Both metals and non-metals are oxidized by concentrated sulphuric acid, which is reduced to  $\text{SO}_2$ .





**Uses:**

- (i) Sulphuric acid is a very important industrial chemical.
- (ii) It is needed for the manufacture of hundreds of other compounds and also in many industrial processes.
- (iii) It is used in the manufacture of fertilizers (Ex: ammonium sulphate, superphosphate).
- (iv) Other uses are in (a) petroleum refining (b) manufacture of pigments, paints, and dyestuff intermediates (c) detergent industry (d) metallurgical applications (e.g., cleansing metals before enameling, electroplating, and galvanizing (e) storage batteries (f) in the manufacture of nitrocellulose products and (g) as a laboratory reagent.

**LECTURE-8****GROUP-17 ELEMENTS:**

Fluorine, chlorine, bromine, iodine, and astatine are members of Group 17. These are collectively known as the halogens (Greek *halo* means salt and *genes* means born i.e., salt producers). The halogens are highly reactive non-metallic elements. Like Groups 1 and 2, the elements of Group 17 show great similarity amongst themselves. Astatine is a radioactive element.

**Occurrence:**

- (i) Fluorine and chlorine are fairly abundant while bromine and iodine less so.
- (ii) Fluorine is present mainly as insoluble fluorides (fluorspar  $\text{CaF}_2$ , cryolite  $\text{Na}_3\text{AlF}_6$ , and fluorapatite  $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaF}_2$ ) and small quantities are present in the soil, river water plants and bones and teeth of animals.
- (iii) Seawater contains chlorides, bromides, and iodides of sodium, potassium, magnesium, and calcium, but is mainly sodium chloride solution (2.5% by mass). The deposits of dried up seas contain these compounds, e.g., sodium chloride and carnallite,  $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ .
- (iv) Certain forms of marine life contain iodine in their systems; various seaweeds, for example, contain up to 0.5% of iodine, and Chile saltpeter contains up to 0.2% of sodium iodate.

**Electronic Configuration:**

All these elements have seven electrons in their outermost shell ( $ns^2np^5$ ) 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 the maximum effective nuclear charge. The atomic radius of fluorine like the other elements of the second period is extremely small. Atomic and ionic radii increase from fluorine to iodine due to the increasing number of quantum shells.

**Ionization Enthalpy:**

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

### **Electron Gain Enthalpy:**

Halogens have maximum negative electron gain enthalpy in the corresponding periods. This is because 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 the small size of the 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.

Q. Halogens have maximum negative electron gain enthalpy in the respective periods of the periodic table. Why?













### **Physical properties:**

- (i) Fluorine and chlorine are gases, bromine is a liquid and iodine is a solid. Their melting and boiling points steadily increase with atomic number.
- (ii) All halogens are colored. This is due to the absorption of radiations in the visible regions which results in the excitation of outer electrons to higher energy levels. By absorbing different quanta of radiation, they display different colors. For example,  $F_2$  has a yellow,  $Cl_2$  greenish-yellow,  $Br_2$  red, and  $I_2$  violet color.
- (iii) Fluorine and chlorine react with water. Bromine and iodine are only sparingly soluble in water but are soluble in various organic solvents such as chloroform, carbon tetrachloride, carbon disulphide, and hydrocarbons to give colored solutions.
- (iv) Enthalpy of dissociation of  $F_2$  is less compared to that of  $Cl_2$ . The X-X bond dissociation enthalpies from chlorine onwards show the expected trend:  $Cl - Cl > Br - Br > I - I$ .
- (v) Low Enthalpy of dissociation is the relatively large electron-electron repulsion among the lone pairs in the  $F_2$  molecule where they are much closer to each other than in the case of  $Cl_2$ .

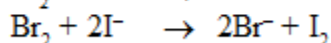
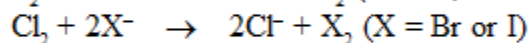
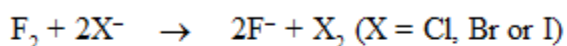
### **CHEMICAL PROPERTIES:**

#### **Oxidation states and trends in chemical reactivity:**

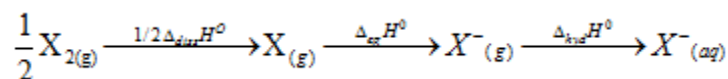
- (i) All the halogens exhibit an  $-1$  oxidation state. However, chlorine, bromine and iodine exhibit  $+1$ ,  $+3$ ,  $+5$  and  $+7$  oxidation states.

|                              |   |   |  |  |
|------------------------------|---|---|--|--|
| <b>Ground state:</b>         | ns<br> | np<br> | nd<br> | one unpaired electron<br>accounts for -1 or +1 O.S |
| <b>First excited state:</b>  | ns<br> | np<br> | nd<br> | 3 unpaired electrons<br>accounts for +3 O.S        |
| <b>Second excited state:</b> | ns<br> | np<br> | nd<br> | 5 unpaired electrons<br>accounts for +5 O.S        |
| <b>Third excited state:</b>  | ns<br> | np<br> | nd<br> | 7 unpaired electrons<br>accounts for +7 O.S        |

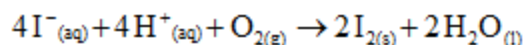
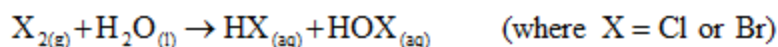
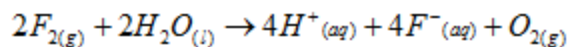
- (ii) The higher oxidation states of chlorine, bromine, and iodine are realized mainly when the halogens are in combination with the small and highly electronegative fluorine and oxygen atoms. e.g., in interhalogens, oxides, and oxoacids.
- (iii) The oxidation states of +4 and +6 occur in the oxides and oxoacids of chlorine and bromine.
- (iv) 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.
- (v) All the halogens are highly reactive. They react with metals and non-metals to form halides.
- (vi) The reactivity of the halogens decreases down the group.
- (vii) The ready acceptance of an electron is the reason for the strong oxidizing nature of halogens.
- (viii)  $F_2$  is the strongest oxidizing halogen and it oxidizes other halide ions in solution or even in the solid phase. In general, a halogen oxidizes halide ions of higher atomic number.



- (ix) The decreasing oxidizing ability of the halogens in aqueous solution down the group is evident from their standard electrode potentials which are dependent on the parameters indicated below:



- (x) The relative oxidizing power of halogens can further be illustrated by their reactions with water. Fluorine oxidizes water to oxygen whereas chlorine and bromine react with water to form corresponding hydrohalic and hypohalous acids. The reaction of iodine with water is nonspontaneous.  $I^-$  can be oxidized by oxygen in an acidic medium; just the reverse of the reaction observed with fluorine.



### **Anomalous behavior of fluorine:**

- (i) Ionization enthalpy, electronegativity, and electrode potentials are all higher for fluorine than other halogens.
- (ii) Ionic and covalent radii, m.p. and b.p., enthalpy of bond dissociation and electron gain enthalpy are quite lower than expected.
- (iii) The anomalous behavior of fluorine is due to its small size, highest electronegativity, low F-F bond dissociation enthalpy, and non-availability of *d*-orbitals in the valence shell.
- (iv) 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 halogens form several oxoacids.
- (v) Hydrogen fluoride is a liquid (b.p. 293 K) due to strong hydrogen bonding. Other hydrogen halides are gases.
- (vi) **Reactivity towards hydrogen:**
  - (a) They all react with hydrogen to give hydrogen halides but the affinity for hydrogen decreases from fluorine to iodine. Hydrogen halides dissolve in water to form hydrohalic acids.
  - (b) The acidic strength of these acids varies in the order: HF < HCl < HBr < HI.
  - (c) The stability of these halides decreases down the group due to a decrease in bond (H-X) dissociation enthalpy in the order: H-F > H-Cl > H-Br > H-I.
- (vii) **Reactivity towards oxygen:**
  - (a) Halogens form many oxides with oxygen but most of them are unstable. Fluorine forms two oxides OF<sub>2</sub> and O<sub>2</sub>F<sub>2</sub>. However, only OF<sub>2</sub> is thermally stable at 298 K.
  - (b) These oxides are essentially oxygen fluorides because of the higher electronegativity of fluorine than oxygen. Both are strong fluorinating agents. O<sub>2</sub>F<sub>2</sub> oxidizes plutonium to PuF<sub>6</sub> and the reaction is used in removing plutonium as PuF<sub>6</sub> from spent nuclear fuel.
  - (c) Chlorine, bromine, and iodine form oxides in which the oxidation states of these halogens range from +1 to +7.
  - (d) A combination of kinetic and thermodynamic factors leads to the generally decreasing order of stability of oxides formed by halogens, I > Cl > Br.
  - (e) The higher oxides of halogens tend to be more stable than the lower ones.
  - (f) Chlorine oxides, Cl<sub>2</sub>O, ClO<sub>2</sub>, Cl<sub>2</sub>O<sub>6</sub>, and Cl<sub>2</sub>O<sub>7</sub> are highly reactive oxidizing agents and tend to explode. ClO<sub>2</sub> is used as a bleaching agent for paper pulp and textiles and in water treatment.
  - (g) The bromine oxides, Br<sub>2</sub>O, BrO<sub>2</sub>, BrO<sub>3</sub> are the least stable halogen oxides (middle row anomaly) and exist only at low temperatures. They are very powerful oxidizing agents.

- (h) The iodine oxides,  $I_2O_4$ ,  $I_2O_5$ ,  $I_2O_7$  are insoluble solids and decompose on heating.  $I_2O_5$  is a very good oxidizing agent and is used in the estimation of carbon monoxide.
- (viii) **Reactivity towards metals:**
- (a) Halogens react with metals to form metal halides. For example, bromine reacts with magnesium to give magnesium bromide.  
 $Mg(s) + Br_2(l) \rightarrow MgBr_2(s)$
- (b) The ionic character of the halides decreases in the order  $MF > MCl > MBr > MI$  where M is a monovalent metal. If a metal exhibits more than one oxidation state, the halides in higher oxidation state will be more covalent than the one in the lower oxidation state.  
Ex:  $SnCl_4$ ,  $PbCl_4$ ,  $SbCl_5$  and  $UF_6$  are more covalent than  $SnCl_2$ ,  $PbCl_2$ ,  $SbCl_3$  and  $UF_4$  respectively.
- (ix) **Reactivity of halogens towards other halogens:**
- (a) Halogens combine amongst themselves to form several compounds known as interhalogens of the types  $XX_2$ ,  $XX_3$ ,  $XX_5$ , and  $XX_7$ . Where X is a larger size halogen and  $X_2$  is a smaller size halogen.

## LECTURE-9

### CHLORINE:

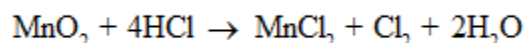
It was discovered in 1774 by Scheele by the action of HCl on  $MnO_2$ . In 1810 Davy established its elementary nature and suggested the name chlorine on account of its color (Greek, *chloros* = greenish-yellow).

#### Preparation:

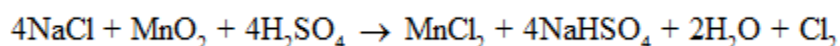
It can be prepared by any one of the following methods:

##### Method-1:

By heating manganese dioxide with concentrated hydrochloric acid.

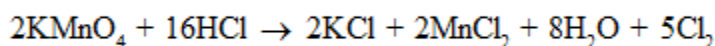


However, a mixture of common salt and concentrated  $H_2SO_4$  is used in place of HCl.



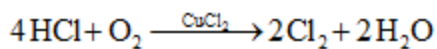
##### Method-2:

By the action of HCl on potassium permanganate.



### Manufacture of chlorine:

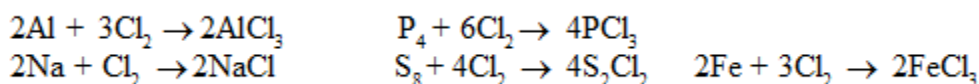
**(i) Deacon's process:** By oxidation of hydrogen chloride gas by atmospheric oxygen in the presence of  $CuCl_2$  (catalyst) at 723 K.



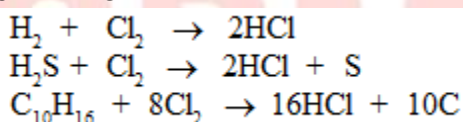
**(ii) Electrolytic process:** Chlorine is obtained by the electrolysis of brine (concentrated NaCl solution). Chlorine is liberated at the anode. It is also obtained as a by-product in many chemical industries.

**Properties:**

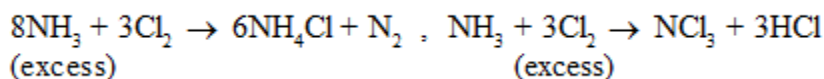
- It is a greenish-yellow gas with a pungent and suffocating odor.
- It is about 2-5 times heavier than air.
- It can be liquefied easily into a greenish-yellow liquid which boils at 239 K.
- It is soluble in water.
- Chlorine reacts with several metals and non-metals to form chlorides.



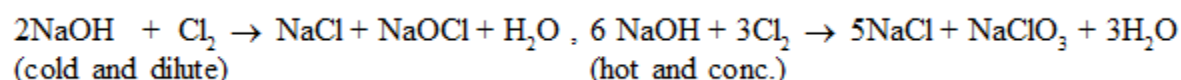
- It has a great affinity for hydrogen. It reacts with compounds containing hydrogen to form HCl.



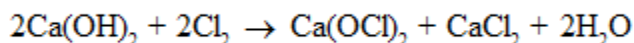
- With excess ammonia, chlorine gives nitrogen and ammonium chloride whereas, with excess chlorine, nitrogen trichloride (explosive) is formed.



- With cold and dilute alkalies chlorine produces a mixture of chloride and hypochlorite but with hot and concentrated alkalies it gives chloride and chlorate.

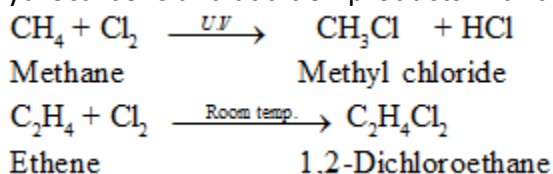


- With dry slaked lime, it gives bleaching powder.

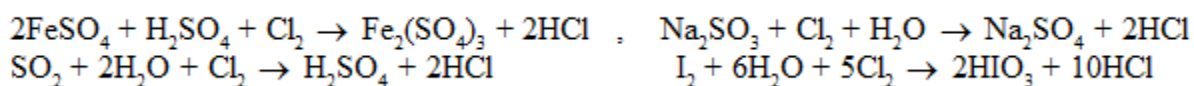


The composition of bleaching powder is  $\text{Ca(OCl)}_2 \cdot \text{CaCl}_2 \cdot \text{Ca(OH)}_2 \cdot 2\text{H}_2\text{O}$ .

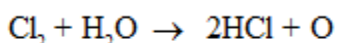
- Chlorine reacts with hydrocarbons and gives substitution products with saturated hydrocarbons and addition products with unsaturated hydrocarbons.



- k) Chlorine water on standing loses its yellow color due to the formation of HCl and HOCl. Hypochlorous acid (HOCl) so formed, gives nascent oxygen which is responsible for oxidizing and bleaching properties of chlorine.
- (l) It oxidizes ferrous to ferric and sulphite to sulphate. Chlorine oxidizes sulphur dioxide to sulphur trioxide and iodine to iodate. In the presence of water, they form sulphuric acid and iodic acid respectively.



- (m) It is a powerful bleaching agent; bleaching action is due to oxidation.



Coloured substance + O → Colourless substance.

It bleaches vegetable or organic matter in the presence of moisture. The bleaching effect of chlorine is permanent.

#### Uses:

It is used

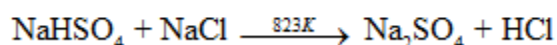
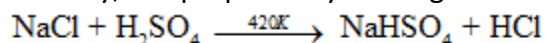
- (i) For bleaching woodpulp (required for the manufacture of paper and rayon), bleaching cotton and textiles.
- (ii) in the extraction of gold and platinum
- (iii) in the manufacture of dyes, drugs and organic compounds such as  $\text{CCl}_4$ ,  $\text{CHCl}_3$ , DDT, refrigerants, etc.
- (iv) in sterilizing drinking water.
- (v) in preparation of poisonous gases such as phosgene ( $\text{COCl}_2$ ), tear gas ( $\text{CCl}_3\text{NO}_2$ ), mustard gas ( $\text{ClCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{Cl}$ ).

#### HYDROGEN CHLORIDE:

Glauber prepared this acid in 1648 by heating common salt with concentrated sulphuric acid. Davy in 1810 showed that it is a compound of hydrogen and chlorine.

#### Preparation:

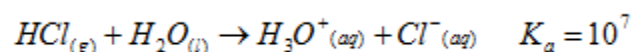
In the laboratory, it is prepared by heating sodium chloride with concentrated sulphuric acid.



HCl gas can be dried by passing through concentrated sulphuric acid.

#### Properties:

- i) It is a colorless and pungent-smelling gas.
- ii) It is easily liquefied to a colorless liquid (b.p.189 K) and freezes to a white crystalline solid (f.p. 159 K).
- iii) It is extremely soluble in water and ionizes as:



- iv) Its aqueous solution is called hydrochloric acid.

- v) A high value of dissociation constant ( $K_a$ ) indicates that it is a strong acid in water.
- vi) It reacts with  $\text{NH}_3$  and gives white fumes of  $\text{NH}_4\text{Cl}$ .  

$$\text{NH}_3 + \text{HCl} \rightarrow \text{NH}_4\text{Cl}$$
- vii) When three parts of concentrated  $\text{HCl}$  and one part of concentrated  $\text{HNO}_3$  are mixed, aqua-regia is formed which is used for dissolving noble metals, e.g., gold, platinum.  

$$\text{Au} + 4\text{H}^+ + \text{NO}_3^- + 4\text{Cl}^- \rightarrow \text{AuCl}_4^- + \text{NO} + 2\text{H}_2\text{O}$$

$$3\text{Pt} + 16\text{H}^+ + 4\text{NO}_3^- + 18\text{Cl}^- \rightarrow 3\text{PtCl}_6^{2-} + 4\text{NO} + 8\text{H}_2\text{O}$$
- viii) Hydrochloric acid decomposes salts of weaker acids, e.g., carbonates, hydrogen carbonates, sulphites, etc.  

$$\text{Na}_2\text{CO}_3 + 2\text{HCl} \rightarrow 2\text{NaCl} + \text{H}_2\text{O} + \text{CO}_2$$

$$\text{NaHCO}_3 + \text{HCl} \rightarrow \text{NaCl} + \text{H}_2\text{O} + \text{CO}_2$$

$$\text{Na}_2\text{SO}_3 + 2\text{HCl} \rightarrow 2\text{NaCl} + \text{H}_2\text{O} + \text{SO}_2$$

**Uses:**

It is used

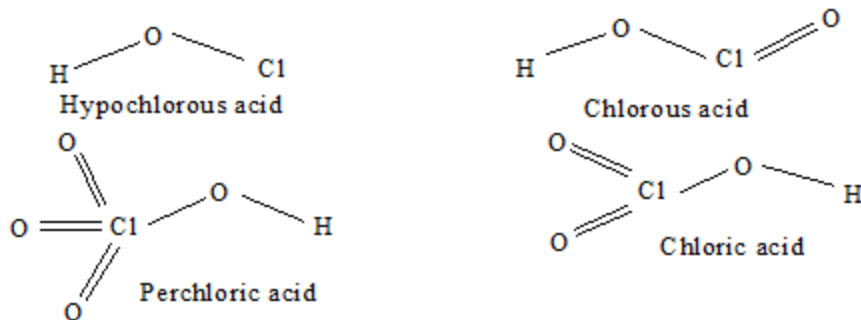
- (i) in the manufacture of chlorine,  $\text{NH}_4\text{Cl}$ , and glucose (from corn starch).
- (ii) for extracting glue from bones and purifying bone black.
- (iii) in medicine and as a laboratory reagent.

**LECTURE-10****OXOACIDS HALOGENS:**

Due to high electronegativity and small size, fluorine forms only one oxoacid,  $\text{HOF}$  known as fluoric (I) acid or hypofluorous acid. The other halogens form several oxoacids. Most of them cannot be isolated in a pure state. They are stable only in aqueous solutions or in the form of their salts.

| Halic (I) acid<br>(Hypohalous acid) | HOF<br>Hypofluorous acid | HOCl<br>Hypochlorous acid               | HOBr<br>Hypobromous acid               | HOI<br>Hypoiodous acid               |
|-------------------------------------|--------------------------|---|--|--------------------------------------|
| Halic (III) acid<br>(Halous acid)   | -                        | HOClO<br>(Chlorous acid)                | -                                      | -                                    |
| Halic (V) acid<br>(Halic acid)      | -                        | HOClO <sub>2</sub><br>(Chloric acid)    | HOBrO <sub>2</sub><br>(Bromic acid)    | HOIO <sub>2</sub><br>(Iodic acid)    |
| Halic (VII) acid<br>(Perhalic acid) | -                        | HOClO <sub>3</sub><br>(Perchloric acid) | HOBrO <sub>3</sub><br>(Perbromic acid) | HOIO <sub>3</sub><br>(Periodic acid) |

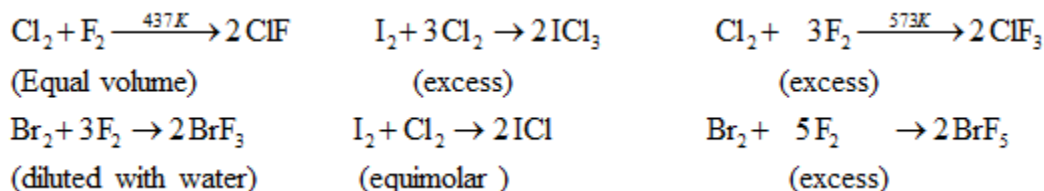


**INTERHALOGEN COMPOUNDS:**

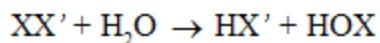
- When two different halogens react with each other, interhalogen compounds are formed.
- They can be assigned general compositions as  $XX'_2$ ,  $XX'_3$ ,  $XX'_5$ , and  $XX'_7$  where X is halogen of larger size and X' of smaller size and X is more electropositive than X'.
- As the ratio between radii of X and X' increases, the number of atoms per molecule also increases. Thus, iodine (VII) fluoride should have a maximum number of atoms as the ratio of radii between I and F should be maximum. That is why its formula is  $IF_7$  (having a maximum number of atoms).

**Preparation:**

The interhalogen compounds can be prepared by the direct combination or by the action of halogen on lower interhalogen compounds. The product formed depends upon some specific conditions.

**Properties:**

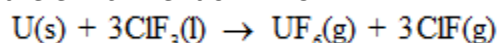
- These are all covalent molecules and are diamagnetic.
- They are volatile solids or liquids at 298 K except for  $ClF$  which is a gas.
- Their physical properties are intermediate between those of constituent halogens except that their m.p. and b.p. are a little higher than expected.
- Their chemical reactions can be compared with the individual halogens. In general, interhalogen compounds are more reactive than halogens (except fluorine). This is because  $X-X'$  bond in interhalogens is weaker than the  $X-X$  bond in halogens except the  $F-F$  bond.
- All these undergo hydrolysis giving halide ion derived from the smaller halogen and a hypohalite (when  $XX'$ ), halite (when  $XX'_3$ ), halite (when  $XX'_5$ ), and perhalate (when  $XX'_7$ ) anion derived from the larger halogen.



- f) Their molecular structures can be explained based on VSEPR theory. The  $XX_3$  Compounds have the bent 'T' shape,  $XX_5$  compounds square pyramidal, and  $IF_7$  has pentagonal bipyramidal structures.

| Type    | Formula   | Physical state and colour   | Structure  |
|---------|---|---|--|
| $XX'_1$ | ClF<br>BrF<br>IF<br>BrCl<br>ICl<br>IBr                                      | Colourless gas<br>Pale brown gas<br>Detected spectroscopically<br>gas<br>ruby red solid( $\alpha$ form), brown red solid( $\beta$ -form)<br>black |  |
| $XX'_3$ | ClF <sub>3</sub><br>BrF <sub>3</sub><br>IF <sub>3</sub><br>ICl <sub>3</sub> | colourless gas<br>yellow green liquid<br>yellow powder<br>orange solid.   | Bent T-shaped<br>Bent T-shaped<br>Bent T-shaped<br>Bent T-shaped |
| $XX'_5$ | IF <sub>5</sub><br>BrF <sub>5</sub><br>ClF <sub>5</sub>                     | colourless gas but solid below 77K<br>colourless liquid<br>colouless liquid   | Square pyramidal<br>Square pyramidal<br>Square pyramidal         |
| $XX'_7$ | IF <sub>7</sub>   | colourless gas  | Pentagonal<br>bipyramidal  |

**Uses:** i) These compounds can be used as non-aqueous solvents. ii) Interhalogen compounds are very useful fluorinating agents. ClF<sub>3</sub> and BrF<sub>3</sub> are used for the production of UF<sub>6</sub> in the enrichment of <sup>235</sup>U.

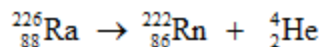


### GROUP-18 ELEMENTS:

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:

- (i) All the noble gases except radon occur in the atmosphere.
- (ii) Their atmospheric abundance in dry air is ~ 1% by volume of which argon is the major constituent.
- (iii) Helium and sometimes neon is found in minerals of radioactive origin e.g., pitchblende, monazite, cleveite. The main commercial source of helium is natural gas.
- (iv) Xenon and radon are the rarest elements of the group. Radon is obtained as a decay product of <sup>226</sup>Ra.

**Electronic Configuration:**

All noble gases have general electronic configuration  $ns^2np^6$  except helium which has  $1s^2$ .

**Ionization Enthalpy:**

Due to stable electronic configuration, these gases exhibit very high I.E. However, it decreases down the group with an increase in atomic size.

**Atomic Radii:**

Atomic radii increase down the group with an increase in atomic number.

**Electron Gain Enthalpy:**

Since noble gases have stable electronic configurations, they have no the tendency to accept the electron and therefore, have large positive values of electron gain enthalpy.

**Physical Properties:**

- (i) All the noble gases are monatomic. They are colorless, odorless, and tasteless.
- (ii) They are sparingly soluble in water.
- (iii) They have very low melting and boiling points because the interatomic interaction in these elements is weak dispersion forces.
- (iv) Helium has the lowest boiling point (4.2 K) of any known substance. It has an unusual property of diffusing through most commonly used laboratory materials such as rubber, glass, or plastics.

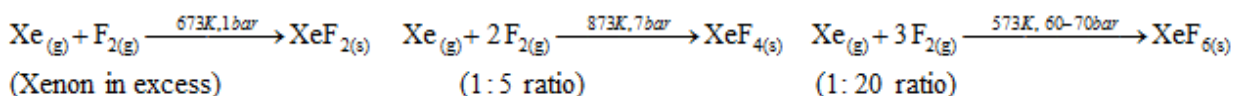
**Chemical Properties:**

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

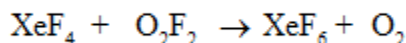
- (i) Except for helium ( $1s^2$ ), all have filled  $ns^2np^6$  configuration in their valence shell.
- (ii) They have high ionization enthalpy and more positive electron gain enthalpy.
- (iii) Neil Bartlett, first, prepared a red compound which is formulated as  $\text{O}_2^+\text{PtF}_6^-$ .
- (iv) He thought that the first ionization enthalpy of molecular oxygen ( $1175 \text{ kJ mol}^{-1}$ ) was almost identical to that of xenon ( $1170 \text{ kJ mol}^{-1}$ ).
- (v) He made efforts to prepare the same type of compound with Xe and was successful in preparing another red color compound  $\text{Xe}^+\text{PtF}_6^-$  by mixing  $\text{PtF}_6$  and xenon.
- (vi) After this discovery, several xenon compounds mainly with most electronegative elements like fluorine and oxygen, have been synthesized.
- (vii) The compounds of krypton are fewer. Only the difluoride ( $\text{KrF}_2$ ) has been studied in detail.
- (viii) Compounds of radon have not been isolated but only identified (e.g.,  $\text{RnF}_2$ ) by radiotracer technique.
- (ix) No true compounds of Ar, Ne, or He are yet known.

**Xenon-fluorine compounds:**

- (i) Xenon forms three binary fluorides,  $\text{XeF}_2$ ,  $\text{XeF}_4$ , and  $\text{XeF}_6$  by the direct reaction of elements under appropriate experimental conditions.



(ii) XeF<sub>6</sub> can also be prepared by the interaction of XeF<sub>4</sub> and O<sub>2</sub>F<sub>2</sub> at 143K.

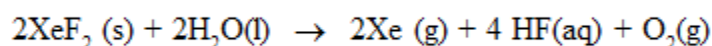


(iii) XeF<sub>2</sub>, XeF<sub>4</sub>, and XeF<sub>6</sub> are colorless crystalline solids and sublime readily at 298 K.

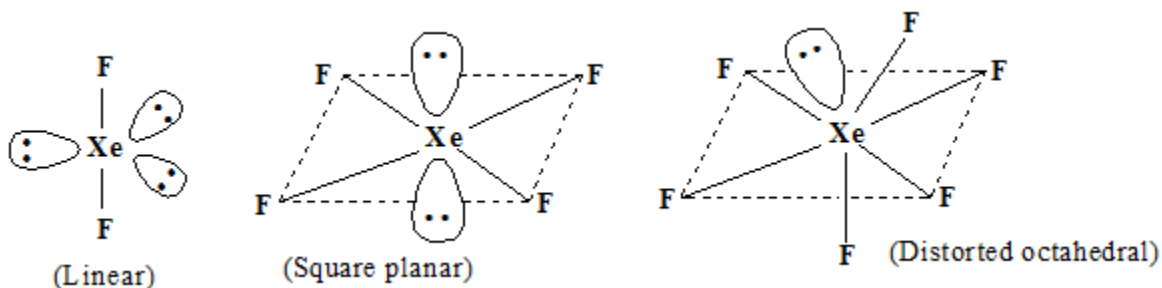
(iv) They are powerful fluorinating agents.

(v) They are readily hydrolyzed even by traces of water.

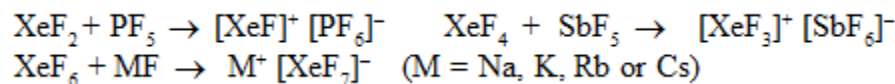
Ex: XeF<sub>2</sub> is hydrolyzed to give Xe, HF, and O<sub>2</sub>.



(vi) The structures of the three xenon fluorides can be deduced from the VSEPR theory. XeF<sub>2</sub> and XeF<sub>4</sub> have linear and square planar structures respectively. XeF<sub>6</sub> has seven electron pairs (6 bonding pairs and one lone pair) and would, thus, have a distorted octahedral structure as found experimentally in the gas phase.

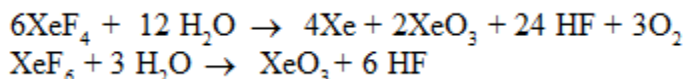


(vii) Xenon fluorides react with fluoride ion acceptors to form cationic species and fluoride ion donors to form fluoroanions.

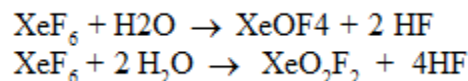


### **(b) Xenon-oxygen compounds:**

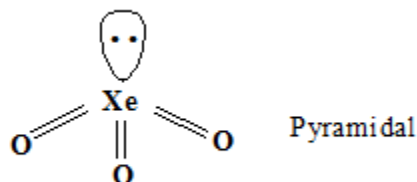
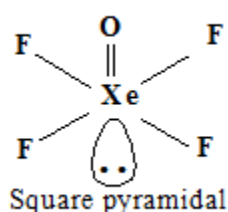
Hydrolysis of XeF<sub>4</sub> and XeF<sub>6</sub> with water gives XeO<sub>3</sub>.



Partial hydrolysis of XeF<sub>6</sub> gives oxyfluorides, XeOF<sub>4</sub> and XeO<sub>2</sub>F<sub>2</sub>.



$\text{XeO}_3$  is a colorless explosive solid and has a pyramidal molecular structure.  $\text{XeOF}_4$  is a colorless volatile liquid and has a square pyramidal molecular structure.



### Uses:

- (i) Helium is a non-inflammable and light gas. Hence, it is used in filling balloons for meteorological observations. It is also used in gas-cooled nuclear reactors. Liquid helium (b.p. 4.2 K) finds use as a 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 diluent for oxygen in the modern diving apparatus because of its very low solubility in blood.
- (ii) Neon is used in discharge tubes and fluorescent bulbs for advertisement display purposes. Neon bulbs are used in botanical gardens and greenhouses.
- (iii) Argon is used mainly to provide an inert atmosphere in high-temperature metallurgical processes (arc welding of metals or alloys) and for filling electric bulbs. It is also used in the laboratory for handling air-sensitive substances.
- (iv) There are no significant uses of Xenon and Krypton. They are used in light bulbs designed for special purposes.

### Answer the following questions: (Lect-1)

1. Though nitrogen exhibits a +5 oxidation state, it does not form pentahalide. Give reason.
2.  $\text{PH}_3$  has a lower boiling point than  $\text{NH}_3$ . Why?
3. Why are pentahalides more covalent than trihalides?
4. Why is  $\text{BiH}_3$  the strongest reducing agent amongst all the hydrides of Group 15 elements?
5. Discuss the general characteristics of Group 15 elements concerning their electronic configuration, oxidation state, atomic size, ionization enthalpy, and electronegativity.
6. Why does the reactivity of nitrogen differ from phosphorus?
7. Discuss the trends in the chemical reactivity of group 15 elements.
8. Why does  $\text{NH}_3$  form hydrogen bond but  $\text{PH}_3$  does not?
9. The HNH angle value is higher than HPH, HAsH, and HSbH angles. Why? [Hint: Can be explained based on  $sp^3$  hybridization in  $\text{NH}_3$  and only  $s-p$  bonding between hydrogen and other elements of the group].
10. Explain why  $\text{NH}_3$  is basic while  $\text{BiH}_3$  is only feebly basic?
11. Nitrogen exists as a diatomic molecule and phosphorus as  $\text{P}_4$ . Why?

12. Why does  $R_3P = O$  exist but  $R_3N = O$  does not (R = alkyl group)?
13. Why does nitrogen show catenation properties less than phosphorus?
14. What are the oxidation states of phosphorus in the following?  
(i)  $H_3PO_3$  (ii)  $PCl_3$  (iii)  $Ca_3P_2$  (iv)  $Na_3PO_4$  (v)  $POF_3$ ?
15. Arrange the following in the order of property indicated for each set:  
 $NH_3$ ,  $PH_3$ ,  $AsH_3$ ,  $SbH_3$ ,  $BiH_3$  – increasing base strength.

**Answer the following questions: (Lect-2)**

1. Why does  $NO_2$  dimerize?
2. What is the covalence of nitrogen in  $N_2O_5$ ?
3. Why does  $NH_3$  act as a Lewis base?
4. Mention the conditions required to maximize the yield of ammonia.
5. How does ammonia react with a solution of  $Cu^{2+}$ ?
6. Write the reaction of the thermal decomposition of sodium azide.
7. Why is nitrogen less reactive at room temperature?
8. How is nitrogen prepared in the laboratory? Write the chemical equations of the reactions involved.
9. How is ammonia manufactured industrially?
10. Give the resonating structures of  $NO_2$  and  $N_2O_5$ .

**Answer the following questions: (Lect-3)**

1. In what way can it be proved that  $PH_3$  is basic?
2. The bond angle in  $PH_4^+$  is higher than that in  $PH_3$ . Why?
3. What happens when white phosphorus is heated with conc. NaOH solution in an inert atmosphere of  $CO_2$ .
4. Write the main differences between the properties of white phosphorus and red phosphorus.
5. Give the disproportionation reaction of  $H_3PO_3$ .
6. How will you prepare nitric acid in the laboratory?
7. Discuss the different steps to prepare nitric acid in Ostwald's process.
8. Name the catalysts used in Ostwald's process.
9. How do Zn and Copper react with concentrated and dilute nitric acid? Write equations.
10. How does conc? Does nitric acid react with non-metals? Give equations.
11. Illustrate how copper metal can give different products on reaction with  $HNO_3$ .

**Answer the following questions: (Lect-4)**

1. How do you account for the reducing behavior of  $H_3PO_2$  based on its structure?
2. Can  $PCl_5$  act as an oxidizing as well as a reducing agent? Justify.
3. Why does  $PCl_5$  fume in moisture?
4. Are all the five bonds in the  $PCl_5$  molecule equivalent? Justify your answer.
5. What happens when  $PCl_5$  is heated?
6. Write a balanced equation for the hydrolytic reaction of  $PCl_5$  in heavy water.

7. What is the basicity of  $\text{H}_3\text{PO}_4$ ?
8. What happens when  $\text{H}_3\text{PO}_3$  is heated?
9. How will you prepare (i)  $\text{H}_3\text{PO}_2$  (ii)  $\text{H}_3\text{PO}_3$  (iii) Pyrophosphorous acid (iv) Orthophosphoric acid (v) Hypophosphoric acid.
10. Draw the structures of Oxoacids of Phosphorus.

**Answer the following questions: (Lect-5)**

1.  $\text{H}_2\text{S}$  is less acidic than  $\text{H}_2\text{Te}$ . Why?
2. List the important sources of sulphur.
3. Write the order of the thermal stability of the hydrides of Group 16 elements.
4. Why is  $\text{H}_2\text{O}$  a liquid and  $\text{H}_2\text{S}$  a gas?
5. Elements of group-16 generally show the lower value of 1st I.E compared to the corresponding periods of group-15. Why?
6. Justify the placement of O, S, Se, Te, and Po in the same group of the periodic table in terms of electronic configuration, oxidation state, and hydride formation.
7. Why is dioxygen a gas but sulphur a solid?
8. Knowing the electron gain enthalpy values for  $\text{O}^-$  and  $\text{O}^{2-}$  as  $-141$  and  $702 \text{ kJ mol}^{-1}$  respectively, how can you account for the formation of a large number of oxides having  $\text{O}^{2-}$  species and not  $\text{O}^-$ ? (Hint: Consider lattice energy factor in the formation of compounds).

**Answer the following questions: (Lect-6)**

1. Which of the following does not react with oxygen directly?  
Zn, Ti, Pt, Fe
2. Complete the following reactions:  
(i)  $\text{C}_2\text{H}_4 + \text{O}_2$  (ii)  $4\text{Al} + 3\text{O}_2$
3. How will you prepare dioxygen from hydrogen peroxide?
4. What happens when pot.chlorate is heated?
5. How will you prepare dioxygen by thermal decomposition of oxides of metals low in the electrochemical series?
6. Classify the following oxides as simple, mixed, acidic, basic, neutral, and amphoteric.  
 $\text{MgO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Pb}_3\text{O}_4$ ,  $\text{Fe}_3\text{O}_4$ ,  $\text{SO}_2$ ,  $\text{Cl}_2\text{O}_7$ ,  $\text{CO}_2$ ,  $\text{N}_2\text{O}_5$ ,  $\text{Mn}_2\text{O}_7$ ,  $\text{CrO}_3$ ,  $\text{V}_2\text{O}_5$ ,  $\text{Na}_2\text{O}$ ,  $\text{CaO}$ ,  $\text{BaO}$ ,  $\text{CO}$ ,  $\text{NO}$ ,  $\text{N}_2\text{O}$ .
7. Show with the chemical reaction that  $\text{Al}_2\text{O}_3$  is an amphoteric oxide.

**Answer the following questions: (Lect-7)**

1. What happens when  
(i) Concentrated  $\text{H}_2\text{SO}_4$  is added to calcium fluoride (ii)  $\text{SO}_3$  is passed through water?
2. Mention three areas in which  $\text{H}_2\text{SO}_4$  plays an important role.
3. Write the conditions to maximize the yield of  $\text{H}_2\text{SO}_4$  by the Contact process.
4. Why is  $K_{a2} \ll K_{a1}$  for  $\text{H}_2\text{SO}_4$  in the water?
5. Why does  $\text{O}_3$  act as a powerful oxidizing agent?

6. How is  $O_3$  estimated quantitatively?
7. What happens when sulphur dioxide is passed through an aqueous solution of Fe(III) salt?
8. Comment on the nature of two S–O bonds formed in the  $SO_2$  molecule. Are the two S–O bonds in this molecule equal?
9. How is the presence of  $SO_2$  detected?
10. Which form of sulphur shows paramagnetic behavior?
11. Which aerosols deplete ozone?
12. Describe the manufacture of  $H_2SO_4$  by the contact process?
13. How is  $SO_2$  an air pollutant?

**Answer the following questions: (Lect--8)**

1. Considering the parameters such as bond dissociation enthalpy, electron gain enthalpy, and hydration enthalpy, compare the oxidizing power of  $F_2$  and  $Cl_2$ .
2. Give two examples to show the anomalous behavior of fluorine.
3. Sea is the greatest source of some halogens. Comment.
4. Fluorine exhibits only a –1 oxidation state whereas other halogens exhibit +1, +3, +5, and +7 oxidation states also. Explain.
5. Although electron gain enthalpy of fluorine is less negative as compared to chlorine, fluorine is a stronger oxidizing agent than chlorine. Why?
6. Halogens have maximum negative electron gain enthalpy in the respective periods of the periodic table. Why?
7. Why are halogens strong oxidizing agents?
8. Explain why despite nearly the same electronegativity, nitrogen forms hydrogen bonding while chlorine does not.
9. Arrange the following in the order of property indicated for each set:  
(i)  $F_2$ ,  $Cl_2$ ,  $Br_2$ ,  $I_2$  - increasing bond dissociation enthalpy.  
(ii)  $HF$ ,  $HCl$ ,  $HBr$ ,  $HI$  - increasing acid strength.
10. Why are halogens colored?

**Answer the following questions: (Lect-9)**

1. Write the balanced chemical equation for the reaction of  $Cl_2$  with hot and concentrated  $NaOH$ . Is this reaction disproportionate? Justify.
2. Give the reason for the bleaching action of  $Cl_2$ .
3. Name two poisonous gases which can be prepared from chlorine gas.
4. When  $HCl$  reacts with finely powdered iron, it forms ferrous chloride and not ferric chloride. Why?
5. Write balanced equations for the following:  
(i)  $NaCl$  is heated with sulphuric acid in the presence of  $MnO_2$ .  
(ii) Chlorine gas is passed into a solution of  $NaI$  in water.
6. What happens when manganese dioxide is heated with conc.  $HCl$ ?
7. What happens when pot. permanganate is heated with  $HCl$ ?



- Describe the manufacture of chlorine by Decon's process.
- How will you obtain chlorine from brine solution?
- Write the balanced equation for the reaction of chlorine with cold alkali.
- Write the reaction of excess ammonia with chlorine and excess chlorine with ammonia.
- Write the balanced equation to prepare bleaching powder from slaked lime and chlorine.
- How will you prepare HCl in the laboratory?
- What is aqua-regia? How it reacts with noble metals?
- How does HCl react with sod.carbanate, bicarbonate, and sulphite?
- Write the reactions of  $F_2$  and  $Cl_2$  with water.
- How can you prepare  $Cl_2$  from HCl and HCl from  $Cl_2$ ? Write the reactions only.

**Answer the following questions: (Lect-10)**

- Discuss the molecular shape of  $BrF_3$  based on VSEPR theory.
- Why is ICl more reactive than  $I_2$ ?
- Explain why fluorine forms only one oxoacid, HOF.
- Write two uses of  $ClO_2$ .
- With what neutral molecule is  $ClO^-$  isoelectronic? Is that molecule a Lewis base?
- Why  $ClF_3$  exists but  $FCl_3$  does not?
- Write the order of acidity of perhalic acids.
- What are the interhalogen compounds? Draw the structures, write shapes, hybridization of  $XX'_3$ ,  $XX'_5$ , and  $XX'_7$  type interhalogen compounds.

**Answer the following questions:**

- Why is helium used in the diving apparatus?
- Balance the following equation:  $XeF_6 + H_2O \rightarrow XeO_2F_2 + HF$
- Why has it been difficult to study the chemistry of radon?
- What inspired N. Bartlett for carrying out a reaction between Xe and  $PtF_6$ ?
- How are xenon fluorides  $XeF_2$ ,  $XeF_4$  and  $XeF_6$  obtained?
- With what neutral molecule is  $ClO^-$  isoelectronic? Is that molecule a Lewis base?
- How are  $XeO_3$  and  $XeOF_4$  prepared?
- Which one of the following does not exist?  
(i)  $XeOF_4$  (ii)  $NeF_2$  (iii)  $XeF_2$  (iv)  $XeF_6$
- Give the formula and describe the structure of a noble gas species which is isostructural with: (i)  $ICl_4^-$  (ii)  $IBr_2^-$  (iii)  $BrO_3^-$
- Why do noble gases have comparatively large atomic sizes?
- List the uses of neon and argon gases.