

Unit

7

## The *p*-Block Elements

### Objectives

After studying this Unit, you will be able to

- appreciate general trends in the chemistry of elements of groups 15, 16, 17 and 18;
- learn the preparation, properties and uses of dinitrogen and phosphorus and some of their important compounds;
- describe the preparation, properties and uses of dioxygen and ozone and chemistry of some simple oxides;
- know allotropic forms of sulphur, chemistry of its important compounds and the structures of its oxoacids;
- describe the preparation, properties and uses of chlorine and hydrochloric acid;
- know the chemistry of interhalogens and structures of oxoacids of halogens;
- enumerate the uses of noble gases;
- appreciate the importance of these elements and their compounds in our day to day life.

*Diversity in chemistry is the hallmark of *p*-block elements manifested in their ability to react with the elements of *s*-, *d*- and *f*-blocks as well as with their own.*

In Class XI, you have learnt that the *p*-block elements are placed in groups 13 to 18 of the periodic table. Their valence shell electronic configuration is  $ns^2np^{1-6}$  (except He which has  $1s^2$  configuration). The properties of *p*-block elements like that of others are greatly influenced by atomic sizes, ionisation enthalpy, electron gain enthalpy and electronegativity. The absence of *d*-orbitals in second period and presence of *d* or *d* and *f* orbitals in heavier elements (starting from third period onwards) have significant effects on the properties of elements. In addition, the presence of all the three types of elements; metals, metalloids and non-metals bring diversification in chemistry of these elements.

Having learnt the chemistry of elements of Groups 13 and 14 of the *p*-block of periodic table in Class XI, you will learn the chemistry of the elements of subsequent groups in this Unit.

### 7.1 Group 15 Elements

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

#### 7.1.1 Occurrence

Molecular nitrogen comprises 78% by volume of the atmosphere. In the earth's crust, it occurs as sodium nitrate,  $\text{NaNO}_3$  (called Chile saltpetre) and potassium nitrate (Indian saltpetre). It is found in the form of proteins in plants and animals. 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. Phosphorus is an essential constituent of animal and plant matter. It is present in bones as well as in living cells. Phosphoproteins are present in milk and eggs. Arsenic, antimony and bismuth are found mainly as sulphide minerals.

The important atomic and physical properties of this group elements along with their electronic configurations are given in Table 7.1.

**Table 7.1: Atomic and Physical Properties of Group 15 Elements**

| Property   | N                     | P                     | As                           | Sb                           | Bi                                  |      |
|--|-----------------------|-----------------------|------------------------------|------------------------------|-------------------------------------|------|
| Atomic number  | 7                     | 15                    | 33                           | 51                           | 83                                  |      |
| Atomic mass/ $\text{g mol}^{-1}$                               | 14.01                 | 30.97                 | 74.92                        | 121.75                       | 208.98                              |      |
| Electronic configuration                                       | $[\text{He}]2s^22p^3$ | $[\text{Ne}]3s^23p^3$ | $[\text{Ar}]3d^{10}4s^24p^3$ | $[\text{Kr}]4d^{10}5s^25p^3$ | $[\text{Xe}]4f^{14}5d^{10}6s^26p^3$ |      |
| Ionisation enthalpy<br>( $\Delta_i H / (\text{kJ mol}^{-1})$ ) | I                     | 1402                  | 1012                         | 947                          | 834                                 | 703  |
|  | II                    | 2856                  | 1903                         | 1798                         | 1595                                | 1610 |
|  | III                   | 4577                  | 2910                         | 2736                         | 2443                                | 2466 |
| Electronegativity  | 3.0                   | 2.1                   | 2.0                          | 1.9                          | 1.9                                 |      |
| Covalent radius/ $\text{pm}^a$                                 | 70                    | 110                   | 121                          | 141                          | 148                                 |      |
| Ionic radius/ $\text{pm}$                                      | 171 <sup>b</sup>      | 212 <sup>b</sup>      | 222 <sup>b</sup>             | 76 <sup>c</sup>              | 103 <sup>c</sup>                    |      |
| Melting point/K  | 63*                   | 317 <sup>d</sup>      | 1089 <sup>e</sup>            | 904                          | 544                                 |      |
| Boiling point/K  | 77.2*                 | 554 <sup>d</sup>      | 888 <sup>f</sup>             | 1860                         | 1837                                |      |
| Density/ $[\text{g cm}^{-3}(\text{298 K})]$                    | 0.879 <sup>g</sup>    | 1.823                 | 5.778 <sup>h</sup>           | 6.697                        | 9.808                               |      |

<sup>a</sup>  $E^{\text{III}}$  single bond ( $E = \text{element}$ ); <sup>b</sup>  $E^{3-}$ ; <sup>c</sup>  $E^{3+}$ ; <sup>d</sup> White phosphorus; <sup>e</sup> Grey  $\alpha$ -form at 38.6 atm; <sup>f</sup> Sublimation temperature; <sup>g</sup> At 63 K; <sup>h</sup> Grey  $\alpha$ -form; \* Molecular  $\text{N}_2$ .

Trends of some of the atomic, physical and chemical properties of the group are discussed below.

### 7.1.2 Electronic Configuration

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

### 7.1.3 Atomic and Ionic Radii

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

### 7.1.4 Ionisation Enthalpy

Ionisation enthalpy decreases down the group due to gradual increase in atomic size. Because of the extra stable half-filled  $p$  orbitals electronic configuration and smaller size, the ionisation enthalpy of the group 15 elements is much greater than that of group 14 elements in the corresponding periods. The order of successive ionisation enthalpies, as expected is  $\Delta_i H_1 < \Delta_i H_2 < \Delta_i H_3$  (Table 7.1).

### 7.1.5 Electronegativity

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

### 7.1.6 Physical Properties

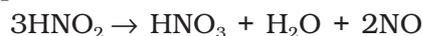
All the elements of this group are polyatomic. Dinitrogen is a diatomic gas while all others are solids. Metallic character increases down the group. Nitrogen and phosphorus are non-metals, arsenic and antimony metalloids and bismuth is a metal. This is due to decrease in ionisation enthalpy and increase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

### 7.1.7 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 increase in size and metallic character. In fact last member of the group, bismuth hardly forms any compound in -3 oxidation state. The stability of +5 oxidation state decreases down the group. The only well characterised Bi (V) compound is  $\text{BiF}_5$ . The stability of +5 oxidation state decreases and that of +3 state increases (due to inert pair effect) down the group. Nitrogen exhibits +1, +2, +4 oxidation states also when it reacts with oxygen. 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,



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

Nitrogen is restricted to a maximum covalency of 4 since only four (one *s* and three *p*) orbitals are available for bonding. The heavier elements have vacant *d* orbitals in the outermost shell which can be used for bonding (covalency) and hence, expand their covalence as in  $\text{PF}_6^-$ .

#### *Anomalous properties of nitrogen*

Nitrogen differs from the rest of the members of this group due to its small size, high electronegativity, high ionisation enthalpy and non-availability of *d* orbitals. Nitrogen has unique ability to form ***pπ-pπ multiple*** bonds with itself and with other elements having small size and high electronegativity (e.g., C, O). Heavier elements of this group do not form *pπ-pπ* bonds as their atomic orbitals are so large and diffuse that they cannot have effective overlapping. Thus, nitrogen exists as a diatomic molecule with a triple bond (one *s* and two *p*) between the two atoms. Consequently, its bond enthalpy ( $941.4 \text{ kJ mol}^{-1}$ ) is very high. On the contrary, phosphorus, arsenic and antimony form single bonds as P-P, As-As and Sb-Sb while bismuth forms metallic bonds in elemental state. However, the single N-N bond is weaker than the single P-P bond because of high interelectronic repulsion of the non-bonding electrons, owing to the small bond length. As a result the catenation tendency is weaker in

nitrogen. Another factor which affects the chemistry of nitrogen is the absence of  $d$  orbitals in its valence shell. Besides restricting its covalency to four, nitrogen cannot form  $d\pi-p\pi$  bond as the heavier elements can e.g.,  $R_3P=O$  or  $R_3P=CH_2$  ( $R$  = alkyl group). Phosphorus and arsenic can form  $d\pi-d\pi$  bond also with transition metals when their compounds like  $P(C_2H_5)_3$  and  $As(C_6H_5)_3$  act as ligands.

- (i) *Reactivity towards hydrogen*: All the elements of Group 15 form hydrides of the type  $EH_3$  where  $E = N, P, As, Sb$  or  $Bi$ . Some of the properties of these hydrides are shown in Table 7.2. The hydrides show regular gradation in their properties. The stability of hydrides decreases from  $NH_3$  to  $BiH_3$  which can be observed from their bond dissociation enthalpy. Consequently, the reducing character of the hydrides increases. Ammonia is only a mild reducing agent while  $BiH_3$  is the strongest reducing agent amongst all the hydrides. Basicity also decreases in the order  $NH_3 > PH_3 > AsH_3 > SbH_3 \geq BiH_3$ .

**Table 7.2: Properties of Hydrides of Group 15 Elements**

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

- (ii) *Reactivity towards oxygen*: All these elements form two types of oxides:  $E_2O_3$  and  $E_2O_5$ . The oxide in the higher oxidation state of the element is more acidic than that of lower oxidation state. Their acidic character decreases down the group. The oxides of the type  $E_2O_3$  of nitrogen and phosphorus are purely acidic, that of arsenic and antimony amphoteric and those of bismuth predominantly basic.
- (iii) *Reactivity towards halogens*: These elements react to form two series of halides:  $EX_3$  and  $EX_5$ . Nitrogen does not form pentahalide due to non-availability of the  $d$  orbitals in its valence shell. Pentahalides are more covalent than trihalides. All the trihalides of these elements except those of nitrogen are stable. In case of nitrogen, only  $NF_3$  is known to be stable. Trihalides except  $BiF_3$  are predominantly covalent in nature.
- (iv) *Reactivity towards metals*: 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).

Though nitrogen exhibits +5 oxidation state, it does not form pentahalide. Give reason.

[Example 7.1](#)

Nitrogen with  $n = 2$ , has  $s$  and  $p$  orbitals only. It does not have  $d$  orbitals to expand its covalence beyond four. That is why it does not form pentahalide.

[Solution](#)

$\text{PH}_3$  has lower boiling point than  $\text{NH}_3$ . Why?

[Example 7.2](#)

Unlike  $\text{NH}_3$ ,  $\text{PH}_3$  molecules are not associated through hydrogen bonding in liquid state. That is why the boiling point of  $\text{PH}_3$  is lower than  $\text{NH}_3$ .

[Solution](#)

### Intext Questions

7.1 Why are pentahalides more covalent than trihalides ?

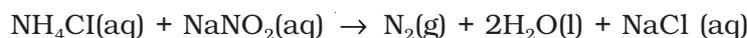
7.2 Why is  $\text{BiH}_3$  the strongest reducing agent amongst all the hydrides of Group 15 elements ?

## 7.2 Dinitrogen

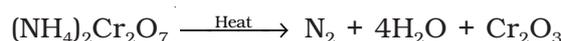
### Preparation

Dinitrogen is produced commercially by the liquefaction and fractional distillation of air. Liquid dinitrogen (b.p. 77.2 K) distils out first leaving behind liquid oxygen (b.p. 90 K).

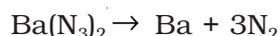
In the laboratory, dinitrogen is prepared by treating an aqueous solution of ammonium chloride with sodium nitrite.



Small amounts of  $\text{NO}$  and  $\text{HNO}_3$  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.



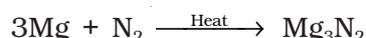
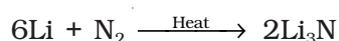
Very pure nitrogen can be obtained by the thermal decomposition of sodium or barium azide.



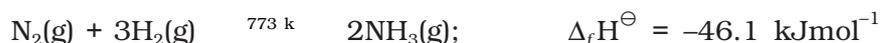
### Properties

Dinitrogen is a colourless, odourless, tasteless and non-toxic gas. Nitrogen atom has two stable isotopes:  $^{14}\text{N}$  and  $^{15}\text{N}$ . It has a very low solubility in water (23.2  $\text{cm}^3$  per litre of water at 273 K and 1 bar pressure) and low freezing and boiling points (Table 7.1).

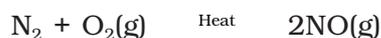
Dinitrogen is rather inert at room temperature because of the high bond enthalpy of  $\text{N}\equiv\text{N}$  bond. Reactivity, however, increases rapidly with rise in temperature. At higher temperatures, it directly combines with some metals to form predominantly ionic nitrides and with non-metals, covalent nitrides. A few typical reactions are:



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



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



**Uses:** The main use of dinitrogen is in the manufacture of ammonia and other industrial chemicals containing nitrogen, (e.g., calcium cyanamide). It also finds use where an inert atmosphere is required (e.g., in iron and steel industry, inert diluent for reactive chemicals). Liquid dinitrogen is used as a refrigerant to preserve biological materials, food items and in cryosurgery.

**Example 7.3** Write the reaction of thermal decomposition of sodium azide.

**Solution** Thermal decomposition of sodium azide gives dinitrogen gas.  

$$2\text{NaN}_3 \rightarrow 2\text{Na} + 3\text{N}_2$$

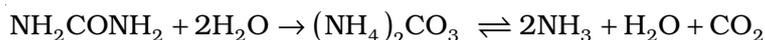
### Intext Question

**7.3** Why is  $\text{N}_2$  less reactive at room temperature?

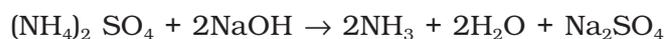
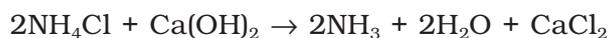
## 7.3 Ammonia

### **Preparation**

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



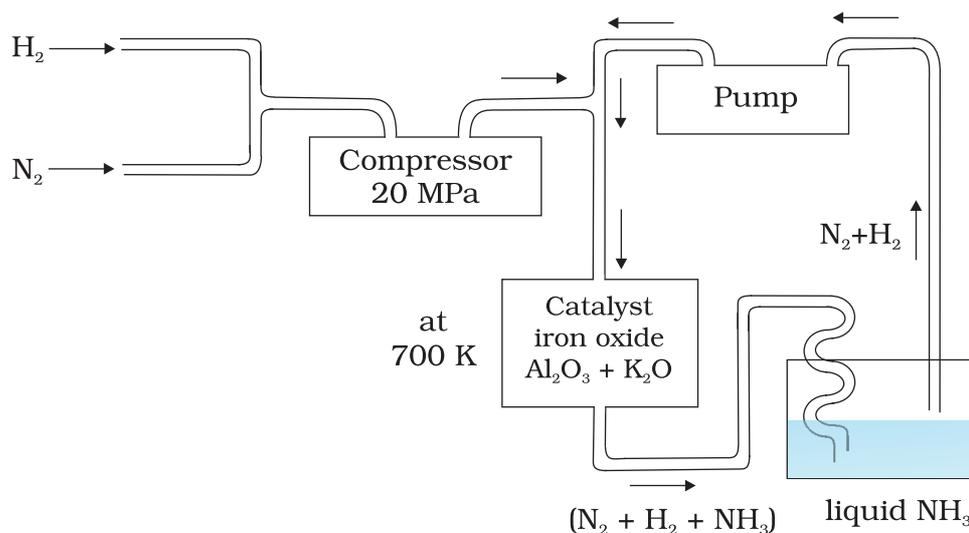
On a small scale ammonia is obtained from ammonium salts which decompose when treated with caustic soda or calcium hydroxide.



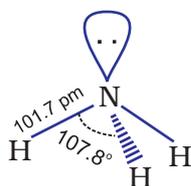
On a large scale, ammonia is manufactured by Haber's process.



In accordance with Le Chatelier's principle, high pressure would favour 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  $\text{K}_2\text{O}$  and  $\text{Al}_2\text{O}_3$  to increase the rate of attainment of equilibrium. The flow chart for the production of ammonia is shown in Fig. 7.1. Earlier, iron was used as a catalyst with molybdenum as a promoter.



**Fig. 7.1**  
Flow chart for the  
manufacture of  
ammonia



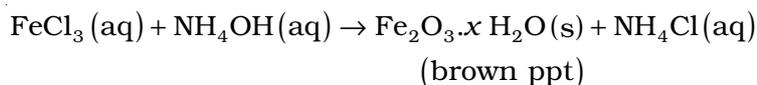
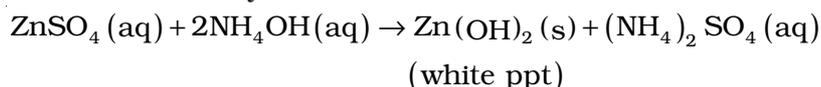
### Properties

Ammonia is a colourless gas with a pungent odour. 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 on the basis of 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 as shown in the structure.

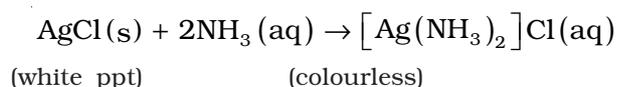
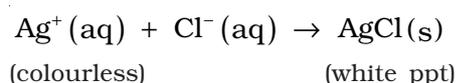
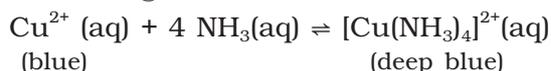
Ammonia gas is highly soluble in water. Its aqueous solution is weakly basic due to the formation of  $\text{OH}^-$  ions.



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,



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  $\text{Cu}^{2+}$ ,  $\text{Ag}^+$ :



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

**Example 7.4** Why does  $\text{NH}_3$  act as a Lewis base ?

**Solution** Nitrogen atom in  $\text{NH}_3$  has one lone pair of electrons which is available for donation. Therefore, it acts as a Lewis base.

### Intext Questions

7.4 Mention the conditions required to maximise the yield of ammonia.

7.5 How does ammonia react with a solution of  $\text{Cu}^{2+}$ ?

## 7.4 Oxides of Nitrogen

Nitrogen forms a number of oxides in different oxidation states. The names, formulas, preparation and physical appearance of these oxides are given in Table 7.3.

**Table 7.3: Oxides of Nitrogen**

| Name   | Formula                | Oxidation state of nitrogen | Common methods of preparation  | Physical appearance and chemical nature |
|--|------------------------|-----------------------------|--|---|
| Dinitrogen oxide<br>[Nitrogen(I) oxide]      | $\text{N}_2\text{O}$   | + 1                         | $\text{NH}_4\text{NO}_3 \xrightarrow{\text{Heat}} \text{N}_2\text{O} + 2\text{H}_2\text{O}$  | colourless gas, neutral                 |
| Nitrogen monoxide<br>[Nitrogen(II) oxide]    | $\text{NO}$            | + 2                         | $2\text{NaNO}_2 + 2\text{FeSO}_4 + 3\text{H}_2\text{SO}_4 \rightarrow \text{Fe}_2(\text{SO}_4)_3 + 2\text{NaHSO}_4 + 2\text{H}_2\text{O} + 2\text{NO}$ | 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                         | $2\text{Pb}(\text{NO}_3)_2 \xrightarrow{673\text{K}} 4\text{NO}_2 + 2\text{PbO} + \text{O}_2$  | 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                          | $4\text{HNO}_3 + \text{P}_4\text{O}_{10} \rightarrow 4\text{HPO}_3 + 2\text{N}_2\text{O}_5$  | colourless solid, acidic                |

Lewis dot main resonance structures and bond parameters of oxides are given in Table 7.4.

**Table 7.4: Structures of Oxides of Nitrogen**

| Formula  | Resonance Structures                                       | Bond Parameters                          |
|----------|--|--|
| $N_2O$   | $\ddot{N}=N=\ddot{O} \leftrightarrow :N\equiv N-\ddot{O}:$ | $N - N - O$<br>113 pm   119 pm<br>Linear |
| $NO$     | $:N = \ddot{O} : \leftrightarrow :\ddot{N} = \ddot{O} :$   | $N - O$<br>115 pm                        |
| $N_2O_3$ |  | <br>Planar                               |
| $NO_2$   |  | <br>Angular                              |
| $N_2O_4$ |  | <br>Planar                               |
| $N_2O_5$ |  | <br>Planar                               |

Why does  $NO_2$  dimerise ?

$NO_2$  contains odd number of valence electrons. It behaves as a typical odd molecule. On dimerisation, it is converted to stable  $N_2O_4$  molecule with even number of electrons.

**Example 7.5**  
**Solution**

### Intext Question

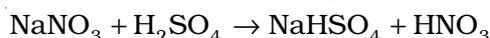
**7.6** What is the covalence of nitrogen in  $N_2O_5$  ?

## 7.5 Nitric Acid

Nitrogen forms oxoacids such as  $H_2N_2O_2$  (hyponitrous acid),  $HNO_2$  (nitrous acid) and  $HNO_3$  (nitric acid). Amongst them  $HNO_3$  is the most important.

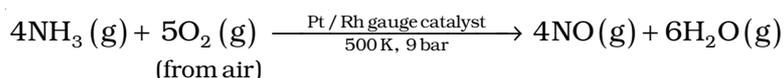
### Preparation

In the laboratory, nitric acid is prepared by heating  $\text{KNO}_3$  or  $\text{NaNO}_3$  and concentrated  $\text{H}_2\text{SO}_4$  in a glass retort.

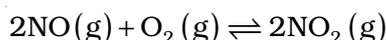


On a large scale it is prepared mainly by Ostwald's process.

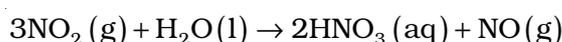
This method is based upon catalytic oxidation of  $\text{NH}_3$  by atmospheric oxygen.



Nitric oxide thus formed combines with oxygen giving  $\text{NO}_2$ .

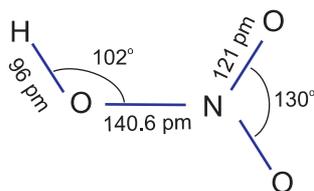


Nitrogen dioxide so formed, dissolves in water to give  $\text{HNO}_3$ .



$\text{NO}$  thus formed is recycled and the aqueous  $\text{HNO}_3$  can be concentrated by distillation upto  $\sim 68\%$  by mass. Further concentration to  $98\%$  can be achieved by dehydration with concentrated  $\text{H}_2\text{SO}_4$ .

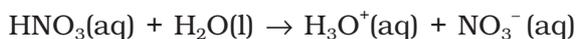
### Properties



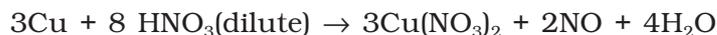
It is a colourless liquid (f.p. 231.4 K and b.p. 355.6 K). Laboratory grade nitric acid contains  $\sim 68\%$  of the  $\text{HNO}_3$  by mass and has a specific gravity of 1.504.

In the gaseous state,  $\text{HNO}_3$  exists as a planar molecule with the structure as shown.

In aqueous solution, nitric acid behaves as a strong acid giving hydronium and nitrate ions.



Concentrated nitric acid is a strong oxidising 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  $\text{NO}_2$ .

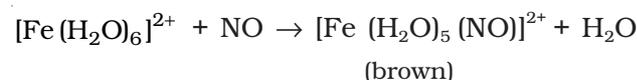
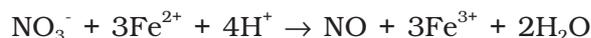


Some metals (e.g., Cr, Al) do not dissolve in concentrated nitric acid because of the formation of a passive film of oxide on the surface.

Concentrated nitric acid also oxidises non-metals and their compounds. Iodine is oxidised to iodic acid, carbon to carbon dioxide, sulphur to  $\text{H}_2\text{SO}_4$ , and phosphorus to phosphoric acid.



**Brown Ring Test:** The familiar 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 coloured complex. The test is usually carried out by adding dilute ferrous sulphate 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.

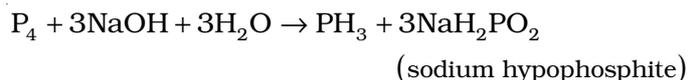


**Uses:** The major use of nitric acid is in the manufacture of ammonium nitrate for fertilisers and other nitrates for use in explosives and pyrotechnics. It is also used for the preparation of nitroglycerin, trinitrotoluene and other organic nitro compounds. Other major uses are in the *pickling of stainless steel*, etching of metals and as an oxidiser in rocket fuels.

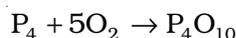
## 7.6 Phosphorus — Allotropic Forms

Phosphorus is found in many allotropic forms, the important ones being white, red and black.

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



White phosphorus is less stable and therefore, more reactive than the other solid phases under normal conditions because of angular strain in the  $\text{P}_4$  molecule where the angles are only  $60^\circ$ . It readily catches fire in air to give dense white fumes of  $\text{P}_4\text{O}_{10}$ .



It consists of discrete tetrahedral  $\text{P}_4$  molecule as shown in Fig. 7.2.

**Red phosphorus** is obtained by heating white phosphorus at 573K in an inert atmosphere for several days. When red phosphorus is heated under high pressure, a series of phases of black phosphorus is formed. Red phosphorus possesses iron grey lustre. It is odourless, non-poisonous and insoluble in water as well as in carbon disulphide. Chemically, red phosphorus is much less reactive than white phosphorus. It does not glow in the dark.

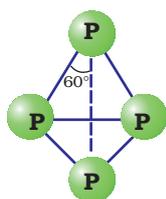


Fig. 7.2  
White phosphorus

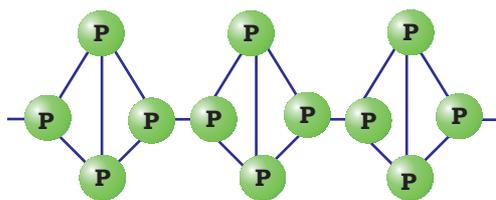


Fig.7.3: Red phosphorus

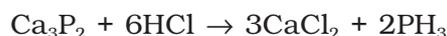
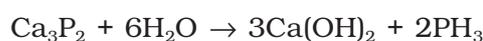
It is polymeric, consisting of chains of P<sub>4</sub> tetrahedra linked together in the manner as shown in Fig. 7.3.

**Black phosphorus** has two forms  $\alpha$ -black phosphorus and  $\beta$ -black phosphorus.  $\alpha$ -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 oxidise in air.  $\beta$ -Black phosphorus is prepared by heating white phosphorus at 473 K under high pressure. It does not burn in air upto 673 K.

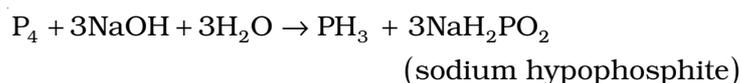
## 7.7 Phosphine

### Preparation

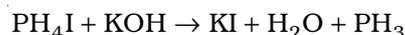
Phosphine is prepared by the reaction of calcium phosphide with water or dilute HCl.



In the laboratory, it is prepared by heating white phosphorus with concentrated NaOH solution in an inert atmosphere of CO<sub>2</sub>.



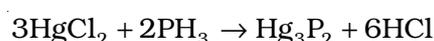
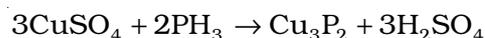
When pure, it is non inflammable but becomes inflammable owing to the presence of P<sub>2</sub>H<sub>4</sub> or P<sub>4</sub> vapours. To purify it from the impurities, it is absorbed in HI to form phosphonium iodide (PH<sub>4</sub>I) which on treating with KOH gives off phosphine.



### Properties

It is a colourless gas with rotten fish smell and is highly poisonous. It explodes in contact with traces of oxidising agents like HNO<sub>3</sub>, Cl<sub>2</sub> and Br<sub>2</sub> vapours.

It is slightly soluble in water. The solution of PH<sub>3</sub> in water decomposes in presence of light giving red phosphorus and H<sub>2</sub>. When absorbed in copper sulphate or mercuric chloride solution, the corresponding phosphides are obtained.



Phosphine is weakly basic and like ammonia, gives phosphonium compounds with acids e.g.,



**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 burn and serve as a signal. It is also used in *smoke screens*.

In what way can it be proved that  $\text{PH}_3$  is basic in nature? **Example 7.6**

$\text{PH}_3$  reacts with acids like HI to form  $\text{PH}_4\text{I}$  which shows that it is basic in nature. **Solution**



Due to lone pair on phosphorus atom,  $\text{PH}_3$  is acting as a Lewis base in the above reaction.

### Intext Questions

7.7 Bond angle in  $\text{PH}_4^+$  is higher than that in  $\text{PH}_3$ . Why?

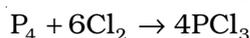
7.8 What happens when white phosphorus is heated with concentrated NaOH solution in an inert atmosphere of  $\text{CO}_2$  ?

**7.8 Phosphorus Halides** Phosphorus forms two types of halides,  $\text{PX}_3$  ( $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$ ) and  $\text{PX}_5$  ( $\text{X} = \text{F}, \text{Cl}, \text{Br}$ ).

#### 7.8.1 Phosphorus Trichloride

##### Preparation

It is obtained by passing dry chlorine over heated white phosphorus.

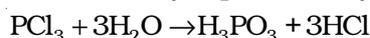


It is also obtained by the action of thionyl chloride with white phosphorus.

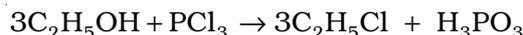
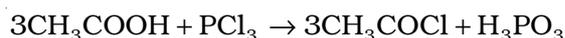


##### Properties

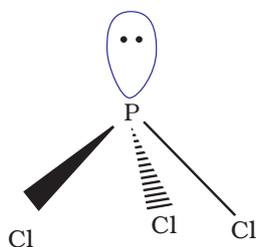
It is a colourless oily liquid and hydrolyses in the presence of moisture.



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



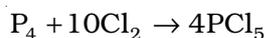
It has a pyramidal shape as shown, in which phosphorus is  $sp^3$  hybridised.



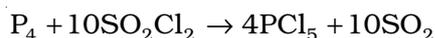
#### 7.8.2 Phosphorus Pentachloride

##### Preparation

Phosphorus pentachloride is prepared by the reaction of white phosphorus with excess of dry chlorine.

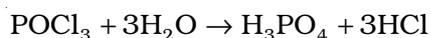
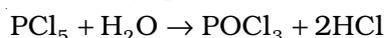


It can also be prepared by the action of  $\text{SO}_2\text{Cl}_2$  on phosphorus.

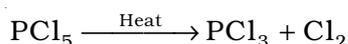


##### Properties

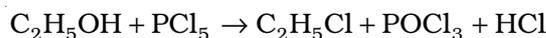
$\text{PCl}_5$  is a yellowish white powder and in moist air, it hydrolyses to  $\text{POCl}_3$  and finally gets converted to phosphoric acid.



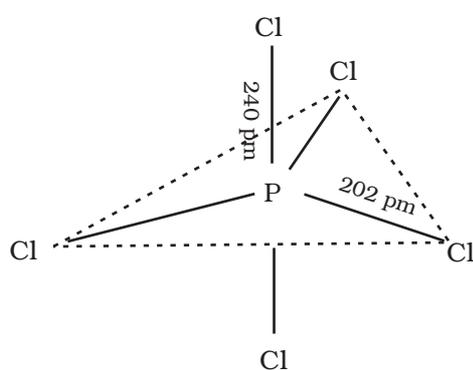
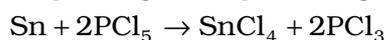
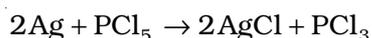
When heated, it sublimes but decomposes on stronger heating.



It reacts with organic compounds containing –OH group converting them to chloro derivatives.



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



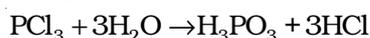
It is used in the synthesis of some organic compounds, e.g.,  $\text{C}_2\text{H}_5\text{Cl}$ ,  $\text{CH}_3\text{COCl}$ .

In gaseous and liquid phases, it has a trigonal bipyramidal structure as shown. The three equatorial P–Cl bonds are equivalent, while the two axial bonds are longer than equatorial bonds. This is due to the fact that the axial bond pairs suffer more repulsion as compared to equatorial bond pairs.

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.

**Example 7.7** Why does  $\text{PCl}_3$  fume in moisture ?

**Solution**  $\text{PCl}_3$  hydrolyses in the presence of moisture giving fumes of  $\text{HCl}$ .



**Example 7.8** Are all the five bonds in  $\text{PCl}_5$  molecule equivalent? Justify your answer.

**Solution**  $\text{PCl}_5$  has a trigonal bipyramidal structure and the three equatorial P–Cl bonds are equivalent, while the two axial bonds are different and longer than equatorial bonds.

### Intext Questions

**7.9** What happens when  $\text{PCl}_5$  is heated?

**7.10** Write a balanced equation for the hydrolytic reaction of  $\text{PCl}_5$  in heavy water.

## 7.9 Oxoacids of Phosphorus

Phosphorus forms a number of oxoacids. The important oxoacids of phosphorus with their formulas, methods of preparation and the presence of some characteristic bonds in their structures are given in Table 7.5.

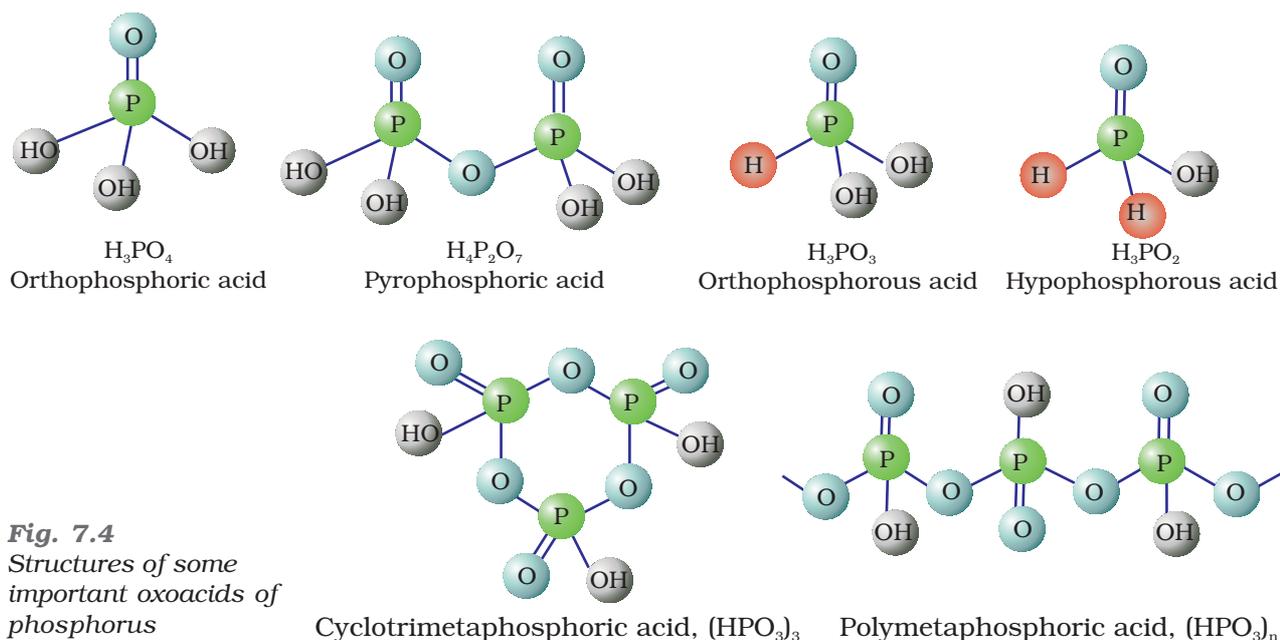
**Table 7.5: Oxoacids of Phosphorus**

| Name                          | Formula     | Oxidation state of phosphorus | Characteristic bonds and their number          | Preparation                                      |
|-------------------------------|-------------|-------------------------------|--|--|
| Hypophosphorous (Phosphinic)  | $H_3PO_2$   | +1                            | One P – OH<br>Two P – H<br>One P = O           | white $P_4$ + alkali                             |
| Orthophosphorous (Phosphonic) | $H_3PO_3$   | +3                            | Two P – OH<br>One P – H<br>One P = O           | $P_2O_3 + H_2O$                                  |
| Pyrophosphorous               | $H_4P_2O_5$ | +3                            | Two P – OH<br>Two P – H<br>Two P = O           | $PCl_3 + H_3PO_3$                                |
| Hypophosphoric                | $H_4P_2O_6$ | +4                            | Four P – OH<br>Two P = O<br>One P – P          | red $P_4$ + alkali                               |
| Orthophosphoric               | $H_3PO_4$   | +5                            | Three P – OH<br>One P = O                      | $P_4O_{10} + H_2O$                               |
| Pyrophosphoric                | $H_4P_2O_7$ | +5                            | Four P – OH<br>Two P = O<br>One P – O – P      | heat phosphoric acid                             |
| Metaphosphoric*               | $(HPO_3)_n$ | +5                            | Three P – OH<br>Three P = O<br>Three P – O – P | phosphorus acid + $Br_2$ , heat in a sealed tube |

\* Exists in polymeric forms only. Characteristic bonds of  $(HPO_3)_3$  have been given in the Table.

The compositions of the oxoacids are interrelated in terms of loss or gain of  $H_2O$  molecule or O-atom.

The structures of some important oxoacids are given below:

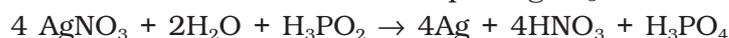


**Fig. 7.4**  
Structures of some important oxoacids of phosphorus

In oxoacids phosphorus is tetrahedrally surrounded by other atoms. All these acids contain at least one P=O bond and one P–OH bond. The oxoacids in which phosphorus has lower oxidation state (less than +5) contain, in addition to P=O and P–OH bonds, either P–P (e.g., in  $\text{H}_4\text{P}_2\text{O}_6$ ) or P–H (e.g., in  $\text{H}_3\text{PO}_2$ ) bonds but not both. These acids in +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.



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,  $\text{AgNO}_3$  to metallic silver.



These P–H bonds are not ionisable to give  $\text{H}^+$  and do not play any role in basicity. Only those H atoms which are attached with oxygen in P–OH form are ionisable and cause the basicity. Thus,  $\text{H}_3\text{PO}_3$  and  $\text{H}_3\text{PO}_4$  are dibasic and tribasic, respectively as the structure of  $\text{H}_3\text{PO}_3$  has two P–OH bonds and  $\text{H}_3\text{PO}_4$  three.

**Example 7.9** How do you account for the reducing behaviour of  $\text{H}_3\text{PO}_2$  on the basis of its structure ?

**Solution** In  $\text{H}_3\text{PO}_2$ , two H atoms are bonded directly to P atom which imparts reducing character to the acid.

### Intext Questions

**7.11** What is the basicity of  $\text{H}_3\text{PO}_4$ ?

**7.12** What happens when  $\text{H}_3\text{PO}_3$  is heated?

## 7.10 Group 16 Elements

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

**7.10.1 Occurrence** 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.

However, the abundance of sulphur in the earth's crust is only 0.03-0.1%. Combined sulphur exists primarily as sulphates such as *gypsum*  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , *epsom salt*  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , *baryte*  $\text{BaSO}_4$  and sulphides such as *galena*  $\text{PbS}$ , *zinc blende*  $\text{ZnS}$ , *copper pyrites*  $\text{CuFeS}_2$ . Traces of sulphur occur as hydrogen sulphide in volcanoes. Organic materials such as eggs, proteins, garlic, onion, mustard, hair and wool contain sulphur.

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

The important atomic and physical properties of Group 16 along with electronic configuration are given in Table 7.6. Some of the atomic, physical and chemical properties and their trends are discussed below.

- 7.10.2 Electronic Configuration** The elements of Group 16 have six electrons in the outermost shell and have  $ns^2np^4$  general electronic configuration.
- 7.10.3 Atomic and Ionic Radii** Due to increase in the number of shells, atomic and ionic radii increase from top to bottom in the group. The size of oxygen atom is, however, exceptionally small.
- 7.10.4 Ionisation Enthalpy** Ionisation enthalpy decreases down the group. It is due to increase in size. However, the elements of this group have lower ionisation enthalpy values compared to those of Group 15 in the corresponding periods. This is due to the fact that Group 15 elements have extra stable half-filled  $p$  orbitals electronic configurations.
- 7.10.5 Electron Gain Enthalpy** Because of the compact nature of oxygen atom, it has less negative electron gain enthalpy than sulphur. However, from sulphur onwards the value again becomes less negative upto polonium.
- 7.10.6 Electronegativity** Next to fluorine, oxygen has the highest electronegativity value amongst the elements. Within the group, electronegativity decreases with an increase in atomic number. This implies that the metallic character increases from oxygen to polonium.

Elements of Group 16 generally show lower value of first ionisation enthalpy compared to the corresponding periods of group 15. Why?

*Example 7.10*

Due to extra stable half-filled  $p$  orbitals electronic configurations of Group 15 elements, larger amount of energy is required to remove electrons compared to Group 16 elements.

*Solution*

- 7.10.7 Physical Properties** Some of the physical properties of Group 16 elements are given in Table 7.6. Oxygen and sulphur are non-metals, selenium and tellurium metalloids, whereas polonium is a metal. Polonium is radioactive and is short lived (Half-life 13.8 days). All these elements exhibit allotropy. The melting and boiling points increase with an increase in atomic number down the group. The large difference between the melting and boiling points of oxygen and sulphur may be explained on the basis of their atomicity; oxygen exists as diatomic molecule ( $O_2$ ) whereas sulphur exists as polyatomic molecule ( $S_8$ ).
- 7.10.8 Chemical Properties** *Oxidation states and trends in chemical reactivity*  
The elements of Group 16 exhibit a number of oxidation states (Table 7.6). The stability of  $-2$  oxidation state decreases down the group. Polonium hardly shows  $-2$  oxidation state. Since electronegativity of oxygen is very high, it shows only negative oxidation state as  $-2$  except

**Table 7.6: Some Physical Properties of Group 16 Elements**

| Property   | O                                   | S                                   | Se   | Te   | Po  |
|--|-------------------------------------|-------------------------------------|--|--|---|
| Atomic number  | 8                                   | 16                                  | 34   | 52   | 84  |
| Atomic mass/g mol <sup>-1</sup>  | 16.00                               | 32.06                               | 78.96  | 127.60   | 210.00  |
| Electronic configuration   | [He]2s <sup>2</sup> 2p <sup>4</sup> | [Ne]3s <sup>2</sup> 3p <sup>4</sup> | [Ar]3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>4</sup> | [Kr]4d <sup>10</sup> 5s <sup>2</sup> 5p <sup>4</sup> | [Xe]4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup> 6p <sup>4</sup> |
| Covalent radius/(pm) <sup>a</sup>  | 66                                  | 104                                 | 117  | 137  | 146   |
| Ionic radius, E <sup>2-</sup> /pm  | 140                                 | 184                                 | 198  | 221  | 230 <sup>b</sup>  |
| Electron gain enthalpy, /Δ <sub>eg</sub> H kJ mol <sup>-1</sup>            | -141                                | -200                                | -195   | -190   | -174  |
| Ionisation enthalpy (Δ <sub>i</sub> H <sub>1</sub> ) /kJ mol <sup>-1</sup> | 1314                                | 1000                                | 941  | 869  | 813   |
| Electronegativity  | 3.50                                | 2.44                                | 2.48   | 2.01   | 1.76  |
| Density /g cm <sup>-3</sup> (298 K)  | 1.32 <sup>c</sup>                   | 2.06 <sup>d</sup>                   | 4.19 <sup>c</sup>                                    | 6.25   | –   |
| Melting point/K  | 55                                  | 393 <sup>f</sup>                    | 490  | 725  | 520   |
| Boiling point/K  | 90                                  | 718                                 | 958  | 1260   | 1235  |
| Oxidation states*  | -2,-1,1,2                           | -2,2,4,6                            | -2,2,4,6   | -2,2,4,6   | 2,4   |

<sup>a</sup>Single bond; <sup>b</sup>Approximate value; <sup>c</sup>At the melting point; <sup>d</sup> Rhombic sulphur; <sup>e</sup>Hexagonal grey; <sup>f</sup>Monoclinic form, 673 K.

\* Oxygen shows oxidation states of +2 and +1 in oxygen fluorides OF<sub>2</sub> and O<sub>2</sub>F<sub>2</sub> respectively.

in the case of OF<sub>2</sub> where its oxidation state is + 2. Other elements of the group exhibit + 2, + 4, + 6 oxidation states but + 4 and + 6 are more common. Sulphur, selenium and tellurium usually show + 4 oxidation state in their compounds with oxygen and + 6 with fluorine. The stability of + 6 oxidation state decreases down the group and stability of + 4 oxidation state increases (inert pair effect). Bonding in +4 and +6 oxidation states is primarily covalent.

#### **Anomalous behaviour of oxygen**

The anomalous behaviour of oxygen, like other members of *p*-block present in second period is due to its small size and high electronegativity. One typical example of effects of small size and high electronegativity is the presence of strong hydrogen bonding in H<sub>2</sub>O which is not found in H<sub>2</sub>S.

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

- (i) **Reactivity with hydrogen:** All the elements of Group 16 form hydrides of the type H<sub>2</sub>E (E = O, S, Se, Te, Po). Some properties of hydrides are given in Table 7.7. Their acidic character increases from H<sub>2</sub>O to H<sub>2</sub>Te. The increase in acidic character can be explained in terms of decrease in bond enthalpy for the dissociation of H–E bond down the group. 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<sub>2</sub>O to H<sub>2</sub>Po. All the hydrides except water possess reducing property and this character increases from H<sub>2</sub>S to H<sub>2</sub>Te.

**Table 7.7: Properties of Hydrides of Group 16 Elements**

| Property  | H <sub>2</sub> O      | H <sub>2</sub> S     | H <sub>2</sub> Se    | H <sub>2</sub> Te    |
|---|-----------------------|----------------------|----------------------|----------------------|
| m.p/K   | 273                   | 188                  | 208                  | 222                  |
| b.p/K   | 373                   | 213                  | 232                  | 269                  |
| H-E distance/pm                                   | 96                    | 134                  | 146                  | 169                  |
| HEH angle (°)                                     | 104                   | 92                   | 91                   | 90                   |
| $\Delta_f H/\text{kJ mol}^{-1}$                   | -286                  | -20                  | 73                   | 100                  |
| $\Delta_{\text{diss}} H (H-E)/\text{kJ mol}^{-1}$ | 463                   | 347                  | 276                  | 238                  |
| Dissociation constant <sup>a</sup>                | $1.8 \times 10^{-16}$ | $1.3 \times 10^{-7}$ | $1.3 \times 10^{-4}$ | $2.3 \times 10^{-3}$ |

<sup>a</sup> Aqueous solution, 298 K

- (ii) *Reactivity with oxygen:* All these elements form oxides of the EO<sub>2</sub> and EO<sub>3</sub> types where E = S, Se, Te or Po. Ozone (O<sub>3</sub>) and sulphur dioxide (SO<sub>2</sub>) are gases while selenium dioxide (SeO<sub>2</sub>) is solid. Reducing property of dioxide decreases from SO<sub>2</sub> to TeO<sub>2</sub>; SO<sub>2</sub> is reducing while TeO<sub>2</sub> is an oxidising agent. Besides EO<sub>2</sub> type, sulphur, selenium and tellurium also form EO<sub>3</sub> type oxides (SO<sub>3</sub>, SeO<sub>3</sub>, TeO<sub>3</sub>). Both types of oxides are acidic in nature.
- (iii) *Reactivity towards the halogens:* Elements of Group 16 form a large number of halides of the type, EX<sub>6</sub>, EX<sub>4</sub> and EX<sub>2</sub> where E is an element of the group and X is a halogen. The stability of the halides decreases in the order F<sup>-</sup> > Cl<sup>-</sup> > Br<sup>-</sup> > I<sup>-</sup>. Amongst hexahalides, hexafluorides are the only stable halides. All hexafluorides are gaseous in nature. They have octahedral structure. Sulphur hexafluoride, SF<sub>6</sub> is exceptionally stable for steric reasons.

Amongst tetrafluorides, SF<sub>4</sub> is a gas, SeF<sub>4</sub> a liquid and TeF<sub>4</sub> a solid. These fluorides have sp<sup>3</sup>d hybridisation 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.

All elements except selenium form dichlorides and dibromides. These dihalides are formed by sp<sup>3</sup> hybridisation and thus, have tetrahedral structure. The well known monohalides are dimeric in nature. Examples are S<sub>2</sub>F<sub>2</sub>, S<sub>2</sub>Cl<sub>2</sub>, S<sub>2</sub>Br<sub>2</sub>, Se<sub>2</sub>Cl<sub>2</sub> and Se<sub>2</sub>Br<sub>2</sub>. These dimeric halides undergo disproportionation as given below:



H<sub>2</sub>S is less acidic than H<sub>2</sub>Te. Why?

*Example 7.11*

Due to the decrease in bond (E-H) dissociation enthalpy down the group, acidic character increases.

*Solution*

### Intext Questions

**7.13** List the important sources of sulphur.

**7.14** Write the order of thermal stability of the hydrides of Group 16 elements.

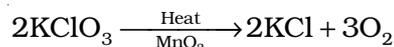
**7.15** Why is H<sub>2</sub>O a liquid and H<sub>2</sub>S a gas ?

## 7.11 Dioxygen

### Preparation

Dioxygen can be obtained in the laboratory by the following ways:

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



- (ii) By the thermal decomposition of the oxides of metals low in the electrochemical series and higher oxides of some metals.



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



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

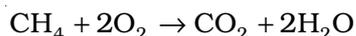
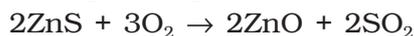
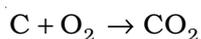
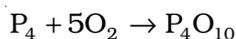
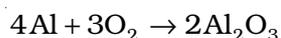
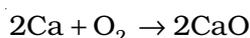
Industrially, dioxygen is obtained from air by first removing carbon dioxide and water vapour and then, the remaining gases are liquefied and fractionally distilled to give dinitrogen and dioxygen.

### Properties

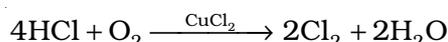
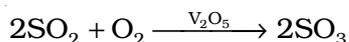
Dioxygen is a colourless and odourless gas. Its solubility in water is to the extent of 3.08 cm<sup>3</sup> in 100 cm<sup>3</sup> water at 293 K which is just sufficient for the vital support of marine and aquatic life. It liquefies at 90 K and freezes at 55 K. Oxygen atom has three stable isotopes: <sup>16</sup>O, <sup>17</sup>O and <sup>18</sup>O. Molecular oxygen, O<sub>2</sub> is unique in being paramagnetic inspite of having even number of electrons (see Class XI Chemistry Book, Unit 4).

Dioxygen directly reacts with nearly all metals and non-metals except some metals (e.g., Au, Pt) and some noble gases. 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 oxygen-oxygen double bond is high (493.4 kJ mol<sup>-1</sup>).

Some of the reactions of dioxygen with metals, non-metals and other compounds are given below:



Some compounds are catalytically oxidised. For example,



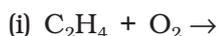
**Uses:** In addition to its importance in normal respiration and combustion processes, oxygen is used in oxyacetylene welding, in the manufacture of many metals, particularly steel. Oxygen cylinders are widely used in hospitals, high altitude flying and in mountaineering. The combustion of fuels, e.g., hydrazines in liquid oxygen, provides tremendous thrust in rockets.

### Intext Questions

**7.16** Which of the following does not react with oxygen directly?

Zn, Ti, Pt, Fe

**7.17** Complete the following reactions:



## 7.12 Simple Oxides

A binary compound of oxygen with another element is called oxide. As already stated, oxygen reacts with most of the elements of the periodic table to form oxides. In many cases one element forms two or more oxides. The oxides vary widely in their nature and properties.

Oxides can be simple (e.g., MgO,  $\text{Al}_2\text{O}_3$ ) or mixed ( $\text{Pb}_3\text{O}_4$ ,  $\text{Fe}_3\text{O}_4$ ). Simple oxides can be classified on the basis of their acidic, basic or amphoteric character. 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  $\text{H}_2\text{SO}_3$ , an acid.

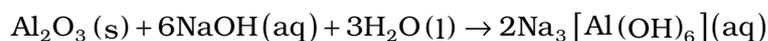
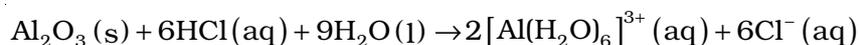


As a general rule, only non-metal oxides are acidic but oxides of some metals in high oxidation state also have acidic character (e.g.,  $\text{Mn}_2\text{O}_7$ ,  $\text{CrO}_3$ ,  $\text{V}_2\text{O}_5$ ). The oxides which give a base with water are known as basic oxides (e.g.,  $\text{Na}_2\text{O}$ ,  $\text{CaO}$ ,  $\text{BaO}$ ). For example,  $\text{CaO}$  combines with water to give  $\text{Ca(OH)}_2$ , a base.



In general, metallic oxides are basic.

Some metallic oxides exhibit a dual behaviour. 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.



There are some oxides which are neither acidic nor basic. Such oxides are known as neutral oxides. Examples of neutral oxides are CO, NO and  $\text{N}_2\text{O}$ .

Ozone is an allotropic form of oxygen. It is too reactive to remain for long in the atmosphere at sea level. At a height of about 20 kilometres, it is formed from atmospheric oxygen in the presence of sunlight. This ozone layer protects the earth's surface from an excessive concentration of ultraviolet (UV) radiations.

## 7.13 Ozone

### 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 ozonised 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.

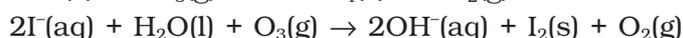
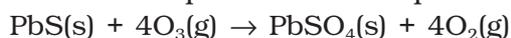
If concentrations of ozone greater than 10 per cent are required, a battery of ozonisers can be used, and pure ozone (b.p. 385 K) can be condensed in a vessel surrounded by liquid oxygen.

### Properties

Pure ozone is a pale blue gas, dark blue liquid and violet-black solid. Ozone has a characteristic smell and in small concentrations it is harmless. However, if the concentration rises above about 100 parts per million, breathing becomes uncomfortable resulting in headache and nausea.

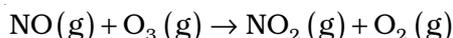
Ozone is thermodynamically unstable with respect to oxygen since its decomposition into oxygen results in the liberation of heat ( $\Delta H$  is negative) and an increase in entropy ( $\Delta S$  is positive). These two effects reinforce each other, resulting in large negative Gibbs energy change ( $\Delta G$ ) for its conversion into oxygen. It is not really surprising, therefore, high concentrations of ozone can be dangerously explosive.

Due to the ease with which it liberates atoms of nascent oxygen ( $\text{O}_3 \rightarrow \text{O}_2 + \text{O}$ ), it acts as a powerful oxidising agent. For example, it oxidises lead sulphide to lead sulphate and iodide ions to iodine.

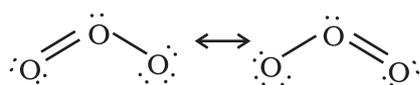


When ozone reacts with an excess of potassium iodide solution buffered with a borate buffer (pH 9.2), iodine is liberated which can be titrated against a standard solution of sodium thiosulphate. This is a quantitative method for estimating  $\text{O}_3$  gas.

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 aeroplanes 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.



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  $117^\circ$ . It is a resonance hybrid of two main forms:

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

### Intext Questions

7.18 Why does  $O_3$  act as a powerful oxidising agent?

7.19 How is  $O_3$  estimated quantitatively?

## 7.14 Sulphur — Allotropic Forms

Sulphur forms numerous allotropes of which the **yellow rhombic** ( $\alpha$ -sulphur) and **monoclinic** ( $\beta$ -sulphur) forms are the most important. The stable form at room temperature is rhombic sulphur, which transforms to monoclinic sulphur when heated above 369 K.

### Rhombic sulphur ( $\alpha$ -sulphur)

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

### Monoclinic sulphur ( $\beta$ -sulphur)

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

Both rhombic and monoclinic sulphur have  $S_8$  molecules. These  $S_8$  molecules are packed to give different crystal structures. The  $S_8$  ring in both the forms is puckered and has a crown shape. The molecular dimensions are given in Fig. 7.5(a).

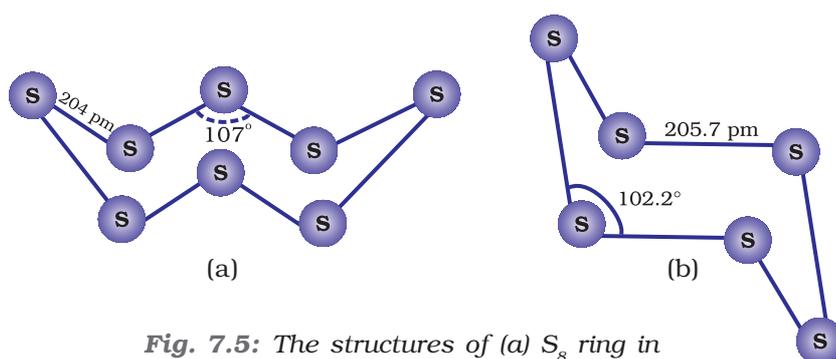


Fig. 7.5: The structures of (a)  $S_8$  ring in rhombic sulphur and (b)  $S_6$  form

Several other modifications of sulphur containing 6-20 sulphur atoms per ring have been synthesised in the last two decades. In cyclo- $S_6$ , the ring adopts the chair form and the molecular dimensions are as shown in Fig. 7.5 (b). At elevated temperatures ( $\sim 1000$  K),  $S_2$  is the dominant species and is paramagnetic like  $O_2$ .

Which form of sulphur shows paramagnetic behaviour ?

In vapour state sulphur partly exists as  $S_2$  molecule which has two unpaired electrons in the antibonding  $\pi^*$  orbitals like  $O_2$  and, hence, exhibits paramagnetism.

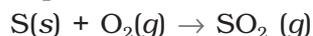
Example 7.12

Solution

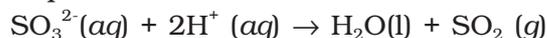
## 7.15 Sulphur Dioxide

### Preparation

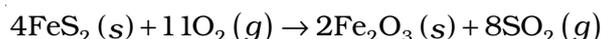
Sulphur dioxide is formed together with a little (6-8%) sulphur trioxide when sulphur is burnt in air or oxygen:



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



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

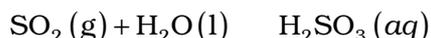


The gas after drying is liquefied under pressure and stored in steel cylinders.

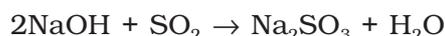
### Properties

Sulphur dioxide is a colourless gas with pungent smell and is highly soluble in water. It liquefies at room temperature under a pressure of two atmospheres and boils at 263 K.

Sulphur dioxide, when passed through water, forms a solution of sulphurous acid.

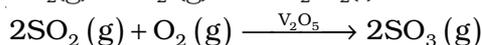
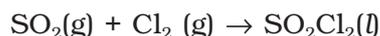


It reacts readily with sodium hydroxide solution, forming sodium sulphite, which then reacts with more sulphur dioxide to form sodium hydrogen sulphite.

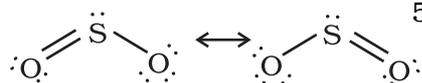
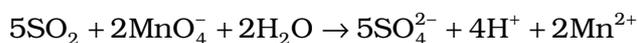
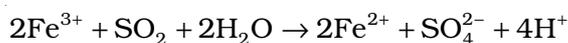


In its reaction with water and alkalis, the behaviour of sulphur dioxide is very similar to that of carbon dioxide.

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 oxidised to sulphur trioxide by oxygen in the presence of vanadium(V) oxide catalyst.



When moist, sulphur dioxide behaves as a reducing agent. For example, it converts iron(III) ions to iron(II) ions and decolourises acidified potassium permanganate(VII) solution; the latter reaction is a convenient test for the gas.



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

**Uses:** Sulphur dioxide is used (i) in refining petroleum and sugar (ii) in bleaching wool and silk and (iii) as an anti-chlor, disinfectant and preservative. Sulphuric 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 a number of organic and inorganic chemicals.

### Intext Questions

- 7.20 What happens when sulphur dioxide is passed through an aqueous solution of Fe(III) salt?
- 7.21 Comment on the nature of two S–O bonds formed in SO<sub>2</sub> molecule. Are the two S–O bonds in this molecule equal ?
- 7.22 How is the presence of SO<sub>2</sub> detected ?

## 7.16 Oxoacids of Sulphur

Sulphur forms a number of oxoacids such as H<sub>2</sub>SO<sub>3</sub>, H<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, H<sub>2</sub>S<sub>2</sub>O<sub>4</sub>, H<sub>2</sub>S<sub>2</sub>O<sub>5</sub>, H<sub>2</sub>S<sub>x</sub>O<sub>6</sub> (x = 2 to 5), H<sub>2</sub>SO<sub>4</sub>, H<sub>2</sub>S<sub>2</sub>O<sub>7</sub>, H<sub>2</sub>SO<sub>5</sub>, H<sub>2</sub>S<sub>2</sub>O<sub>8</sub>. Some of these acids are unstable and cannot be isolated. They are known in aqueous solution or in the form of their salts. Structures of some important oxoacids are shown in Fig. 7.6.

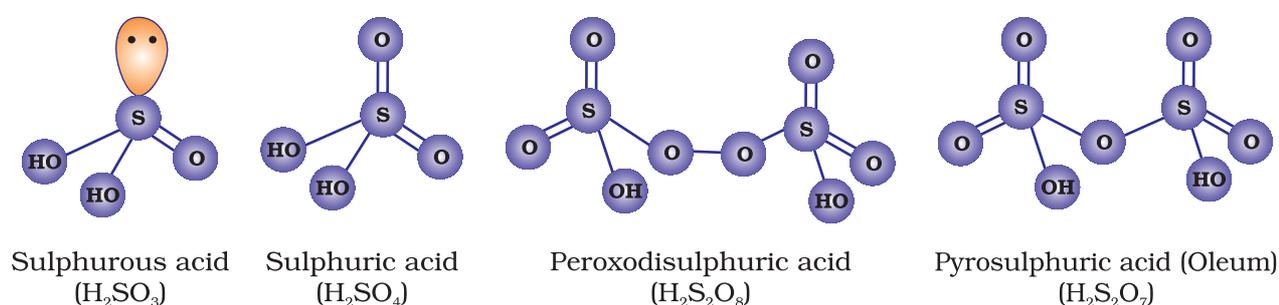


Fig. 7.6: Structures of some important oxoacids of sulphur

## 7.17 Sulphuric Acid

### Manufacture

Sulphuric acid is one of the most important industrial chemicals worldwide.

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

- burning of sulphur or sulphide ores in air to generate SO<sub>2</sub>.
- conversion of SO<sub>2</sub> to SO<sub>3</sub> by the reaction with oxygen in the presence of a catalyst (V<sub>2</sub>O<sub>5</sub>), and
- absorption of SO<sub>3</sub> in H<sub>2</sub>SO<sub>4</sub> to give *Oleum* (H<sub>2</sub>S<sub>2</sub>O<sub>7</sub>).

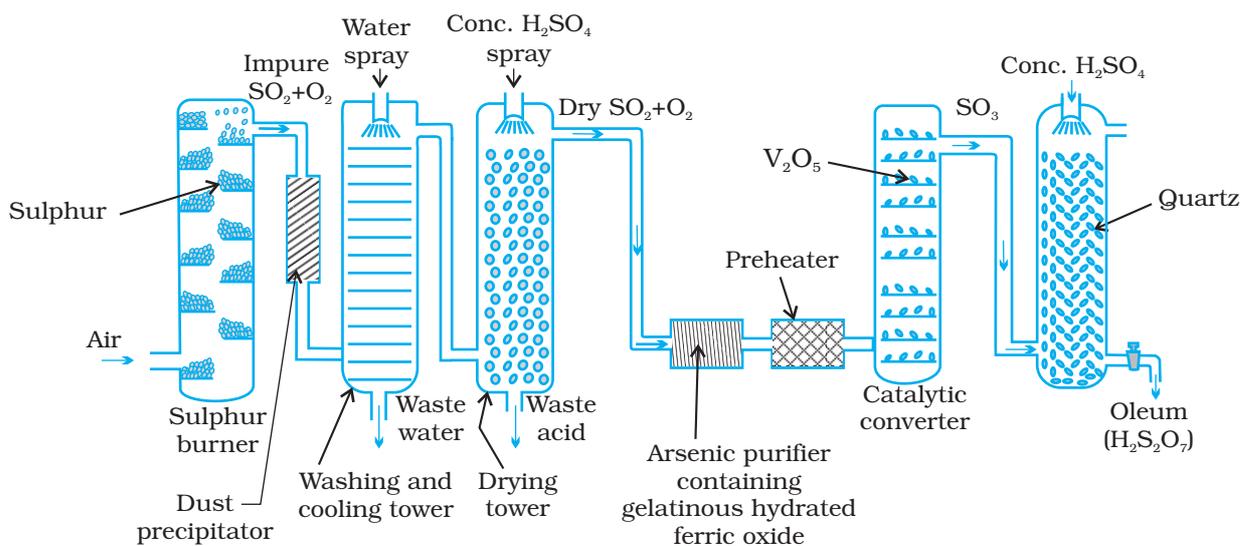
A flow diagram for the manufacture of sulphuric acid is shown in (Fig. 7.7). The SO<sub>2</sub> produced is purified by removing dust and other impurities such as arsenic compounds.

The key step in the manufacture of H<sub>2</sub>SO<sub>4</sub> is the catalytic oxidation of SO<sub>2</sub> with O<sub>2</sub> to give SO<sub>3</sub> in the presence of V<sub>2</sub>O<sub>5</sub> (catalyst).



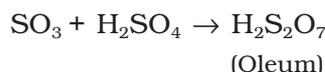
The reaction is exothermic, reversible and the forward reaction leads to a decrease in volume. Therefore, low temperature and high pressure are the favourable conditions for maximum yield. But the temperature should not be very low otherwise rate of reaction will become slow.

In practice, the plant is operated at a pressure of 2 bar and a temperature of 720 K. The SO<sub>3</sub> gas from the catalytic converter is



**Fig. 7.7:** Flow diagram for the manufacture of sulphuric acid

absorbed in concentrated  $\text{H}_2\text{SO}_4$  to produce *oleum*. Dilution of oleum with water gives  $\text{H}_2\text{SO}_4$  of the desired concentration. In the industry two steps are carried out simultaneously to make the process a continuous one and also to reduce the cost.

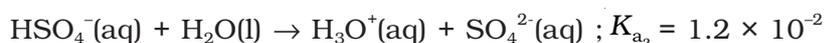


The sulphuric acid obtained by Contact process is 96-98% pure.

### Properties

Sulphuric acid is a colourless, dense, oily liquid with a specific gravity of 1.84 at 298 K. The acid freezes at 283 K and boils at 611 K. It dissolves in water with the evolution of a large quantity of heat. Hence, care must be taken while preparing sulphuric acid solution from concentrated sulphuric acid. The concentrated acid must be added slowly into water with constant stirring.

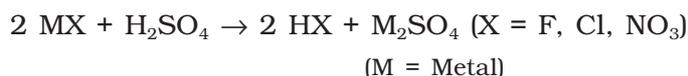
The chemical reactions of sulphuric acid are as a result of the following characteristics: (a) low volatility (b) strong acidic character (c) strong affinity for water and (d) ability to act as an oxidising agent. In aqueous solution, sulphuric acid ionises in two steps.



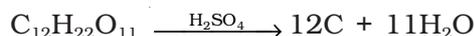
The larger value of  $K_{a_1}$  ( $K_{a_1} > 10$ ) means that  $\text{H}_2\text{SO}_4$  is largely dissociated into  $\text{H}^+$  and  $\text{HSO}_4^-$ . Greater the value of dissociation constant ( $K_a$ ), the stronger is the acid.

The acid forms two series of salts: normal sulphates (such as sodium sulphate and copper sulphate) and acid sulphates (e.g., sodium hydrogen sulphate).

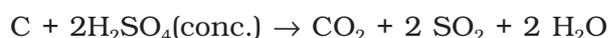
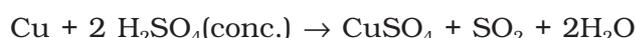
Sulphuric acid, because of its low volatility can be used to manufacture more volatile acids from their corresponding salts.



Concentrated sulphuric acid is a strong dehydrating agent. Many wet gases can be dried by passing them through sulphuric acid, provided the gases do not react with the acid. Sulphuric acid removes water from organic compounds; it is evident by its charring action on carbohydrates.



Hot concentrated sulphuric acid is a moderately strong oxidising agent. In this respect, it is intermediate between phosphoric and nitric acids. Both metals and non-metals are oxidised by concentrated sulphuric acid, which is reduced to  $\text{SO}_2$ .



*Uses:* Sulphuric acid is a very important industrial chemical. A nation's industrial strength can be judged by the quantity of sulphuric acid it produces and consumes. It is needed for the manufacture of hundreds of other compounds and also in many industrial processes. The bulk of sulphuric acid produced is used in the manufacture of fertilisers (e.g., ammonium sulphate, superphosphate). 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 galvanising (e) storage batteries (f) in the manufacture of nitrocellulose products and (g) as a laboratory reagent.

### Intext Questions

- 7.23** Mention three areas in which  $\text{H}_2\text{SO}_4$  plays an important role.
- 7.24** Write the conditions to maximise the yield of  $\text{H}_2\text{SO}_4$  by Contact process.
- 7.25** Why is  $K_{a_2} \ll K_{a_1}$  for  $\text{H}_2\text{SO}_4$  in water ?

## 7.18 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. That much similarity is not found in the elements of other groups of the periodic table. Also, there is a regular gradation in their physical and chemical properties. Astatine is a radioactive element.

### 7.18.1 Occurrence

Fluorine and chlorine are fairly abundant while bromine and iodine less so. Fluorine is present mainly as insoluble fluorides (fluorspar  $\text{CaF}_2$ , cryolite  $\text{Na}_3\text{AlF}_6$  and fluoroapatite  $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaF}_2$ ) and small quantities are present in soil, river water plants and bones and teeth of animals. Sea water 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,  $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ . Certain forms of marine life contain iodine in their systems; various seaweeds, for example, contain upto 0.5% of iodine and Chile saltpetre contains upto 0.2% of sodium iodate.

The important atomic and physical properties of Group 17 elements along with their electronic configurations are given in Table 7.8.

Table 7.8: Atomic and Physical Properties of Halogens

| Property   | F                     | Cl                      | Br                           | I                            | At <sup>a</sup>                     |
|--|-----------------------|-------------------------|------------------------------|------------------------------|-------------------------------------|
| Atomic number  | 9                     | 17                      | 35                           | 53                           | 85                                  |
| Atomic mass/g mol <sup>-1</sup>                      | 19.00                 | 35.45                   | 79.90                        | 126.90                       | 210                                 |
| Electronic configuration                             | $[\text{He}]2s^22p^5$ | $[\text{Ne}]3s^23p^5$   | $[\text{Ar}]3d^{10}4s^24p^5$ | $[\text{Kr}]4d^{10}5s^25p^5$ | $[\text{Xe}]4f^{14}5d^{10}6s^26p^5$ |
| Covalent radius/pm                                   | 64                    | 99                      | 114                          | 133                          | –                                   |
| Ionic radius X <sup>-</sup> /pm                      | 133                   | 184                     | 196                          | 220                          | –                                   |
| Ionisation enthalpy/kJ mol <sup>-1</sup>             | 1680                  | 1256                    | 1142                         | 1008                         | –                                   |
| Electron gain enthalpy/kJ mol <sup>-1</sup>          | -333                  | -349                    | -325                         | -296                         | –                                   |
| Electronegativity <sup>b</sup>                       | 4                     | 3.2                     | 3.0                          | 2.7                          | 2.2                                 |
| $\Delta_{\text{hyd}}H(X^-)/\text{kJ mol}^{-1}$       | 515                   | 381                     | 347                          | 305                          | –                                   |
|  | F <sub>2</sub>        | Cl <sub>2</sub>         | Br <sub>2</sub>              | I <sub>2</sub>               | –                                   |
| Melting point/K                                      | 54.4                  | 172.0                   | 265.8                        | 386.6                        | –                                   |
| Boiling point/K                                      | 84.9                  | 239.0                   | 332.5                        | 458.2                        | –                                   |
| Density/g cm <sup>-3</sup>                           | 1.5 (85) <sup>c</sup> | 1.66 (203) <sup>c</sup> | 3.19(273) <sup>c</sup>       | 4.94(293) <sup>d</sup>       | –                                   |
| Distance X – X/pm                                    | 143                   | 199                     | 228                          | 266                          | –                                   |
| Bond dissociation enthalpy / (kJ mol <sup>-1</sup> ) | 158.8                 | 242.6                   | 192.8                        | 151.1                        | –                                   |
| $E^\ominus/V^e$                                      | 2.87                  | 1.36                    | 1.09                         | 0.54                         | –                                   |

<sup>a</sup> Radioactive; <sup>b</sup> Pauling scale; <sup>c</sup> For the liquid at temperatures (K) given in the parentheses; <sup>d</sup> solid; <sup>e</sup> The half-cell reaction is  $\text{X}_2(\text{g}) + 2\text{e}^- \rightarrow 2\text{X}(\text{aq})$ .

The trends of some of the atomic, physical and chemical properties are discussed below.

- 7.18.2 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.
- 7.18.3 Atomic and Ionic Radii** The halogens have the smallest atomic radii in their respective periods due to maximum effective nuclear charge. The atomic radius of fluorine like the other elements of second period is extremely small. Atomic and ionic radii increase from fluorine to iodine due to increasing number of quantum shells.
- 7.18.4 Ionisation Enthalpy** They have little tendency to lose electron. Thus they have very high ionisation enthalpy. Due to increase in atomic size, ionisation enthalpy decreases down the group.
- 7.18.5 Electron Gain Enthalpy** Halogens have maximum negative electron gain enthalpy in the corresponding periods. This is due to the fact that the atoms of these elements have only one electron less than stable noble gas configurations. Electron gain enthalpy of the elements of the group becomes less negative down the group. However, the negative electron gain enthalpy of fluorine is less than that of chlorine. It is due to small size of fluorine atom. As a result, there are strong interelectronic repulsions in the relatively small  $2p$  orbitals of fluorine and thus, the incoming electron does not experience much attraction.
- 7.18.6 Electronegativity** They have very high electronegativity. The electronegativity decreases down the group. Fluorine is the most electronegative element in the periodic table.

Halogens have maximum negative electron gain enthalpy in the [Example 7.14](#) respective periods of the periodic table. Why?

Halogens have the smallest size in their respective periods and therefore [Solution](#) high effective nuclear charge. As a consequence, they readily accept one electron to acquire noble gas electronic configuration.

- 7.18.7 Physical Properties** Halogens display smooth variations in their physical properties. Fluorine and chlorine are gases, bromine is a liquid and iodine is a solid. Their melting and boiling points steadily increase with atomic number. All halogens are coloured. This is due to absorption of radiations in visible region which results in the excitation of outer electrons to higher energy level. By absorbing different quanta of radiation, they display different colours. For example,  $F_2$ , has yellow,  $Cl_2$ , greenish yellow,  $Br_2$ , red and  $I_2$ , violet colour. Fluorine and chlorine react with water. Bromine and iodine are only sparingly soluble in water but are soluble in various organic solvents such as chloroform, carbon tetrachloride, carbon disulphide and hydrocarbons to give coloured solutions.
- One curious anomaly we notice from Table 7.8 is the smaller enthalpy of dissociation of  $F_2$  compared to that of  $Cl_2$  whereas X-X bond dissociation enthalpies from chlorine onwards show the expected

trend:  $\text{Cl} - \text{Cl} > \text{Br} - \text{Br} > \text{I} - \text{I}$ . A reason for this anomaly is the relatively large electron-electron repulsion among the lone pairs in  $\text{F}_2$  molecule where they are much closer to each other than in case of  $\text{Cl}_2$ .

### Example 7.15

Although electron gain enthalpy of fluorine is less negative as compared to chlorine, fluorine is a stronger oxidising agent than chlorine. Why?

### Solution

It is due to

- (i) low enthalpy of dissociation of F-F bond (Table 7.8).
- (ii) high hydration enthalpy of  $\text{F}^-$  (Table 7.8).

### 7.18.8 Chemical Properties

#### Oxidation states and trends in chemical reactivity

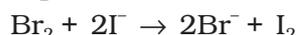
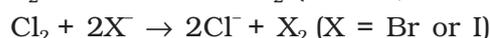
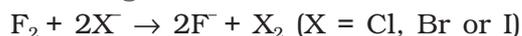
All the halogens exhibit  $-1$  oxidation state. However, chlorine, bromine and iodine exhibit  $+1$ ,  $+3$ ,  $+5$  and  $+7$  oxidation states also as explained below:

| Halogen atom in ground state (other than fluorine) | ns                   | np   | nd   |  |
|--|----------------------|--|--|--|
|  | $\uparrow\downarrow$ | $\uparrow\downarrow \uparrow\downarrow \uparrow$ | $\square \square \square \square \square$    | 1 unpaired electron accounts for $-1$ or $+1$ oxidation states |
| First excited state                                | $\uparrow\downarrow$ | $\uparrow\downarrow \uparrow \uparrow$           | $\uparrow \square \square \square \square$   | 3 unpaired electrons account for $+3$ oxidation states         |
| Second excited state                               | $\uparrow\downarrow$ | $\uparrow \uparrow \uparrow$                     | $\uparrow \uparrow \square \square \square$  | 5 unpaired electrons account for $+5$ oxidation state          |
| Third excited state                                | $\uparrow\downarrow$ | $\uparrow \uparrow \uparrow$                     | $\uparrow \uparrow \uparrow \square \square$ | 7 unpaired electrons account for $+7$ oxidation state          |

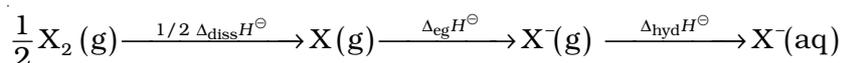
The higher oxidation states of chlorine, bromine and iodine are realised mainly when the halogens are in combination with the small and highly electronegative fluorine and oxygen atoms. e.g., in interhalogens, oxides and oxoacids. The oxidation states of  $+4$  and  $+6$  occur in the oxides and oxoacids of chlorine and bromine. The fluorine atom has no  $d$  orbitals in its valence shell and therefore cannot expand its octet. Being the most electronegative, it exhibits only  $-1$  oxidation state.

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

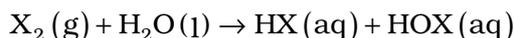
The ready acceptance of an electron is the reason for the strong oxidising nature of halogens.  $\text{F}_2$  is the strongest oxidising halogen and it oxidises other halide ions in solution or even in the solid phase. In general, a halogen oxidises halide ions of higher atomic number.



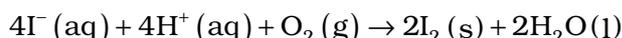
The decreasing oxidising ability of the halogens in aqueous solution down the group is evident from their standard electrode potentials (Table 7.8) which are dependent on the parameters indicated below:



The relative oxidising power of halogens can further be illustrated by their reactions with water. Fluorine oxidises water to oxygen whereas chlorine and bromine react with water to form corresponding hydrohalic and hypohalous acids. The reaction of iodine with water is non-spontaneous. In fact,  $I^-$  can be oxidised by oxygen in acidic medium; just the reverse of the reaction observed with fluorine.



(where X = Cl or Br)



### Anomalous behaviour of fluorine

Like other elements of *p*-block present in second period of the periodic table, fluorine is anomalous in many properties. For example, ionisation enthalpy, electronegativity, and electrode potentials are all higher for fluorine than expected from the trends set by other halogens. Also, ionic and covalent radii, m.p. and b.p., enthalpy of bond dissociation and electron gain enthalpy are quite lower than expected. The anomalous behaviour of fluorine is due to its small size, highest electronegativity, low F-F bond dissociation enthalpy, and non availability of *d* orbitals in valence shell.

Most of the reactions of fluorine are exothermic (due to the small and strong bond formed by it with other elements). It forms only one oxoacid while other halogens form a number of oxoacids. Hydrogen fluoride is a liquid (b.p. 293 K) due to strong hydrogen bonding. Other hydrogen halides are gases.

- (i) *Reactivity towards hydrogen*: They all react with hydrogen to give hydrogen halides but affinity for hydrogen decreases from fluorine to iodine. Hydrogen halides dissolve in water to form hydrohalic acids. Some of the properties of hydrogen halides are given in Table 7.9. The acidic strength of these acids varies in the order: HF < HCl < HBr < HI. The stability of these halides decreases down the group due to decrease in bond (H-X) dissociation enthalpy in the order: H-F > H-Cl > H-Br > H-I.

Table 7.9: Properties of Hydrogen Halides

| Property  | HF   | HCl   | HBr   | HI    |
|---|------|-------|-------|-------|
| Melting point/K                                       | 190  | 159   | 185   | 222   |
| Boiling point/K                                       | 293  | 189   | 206   | 238   |
| Bond length (H - X)/pm                                | 91.7 | 127.4 | 141.4 | 160.9 |
| $\Delta_{\text{diss}} H^\ominus / \text{kJ mol}^{-1}$ | 574  | 432   | 363   | 295   |
| $pK_a$  | 3.2  | -7.0  | -9.5  | -10.0 |

- (ii) *Reactivity towards oxygen*: Halogens form many oxides with oxygen but most of them are unstable. Fluorine forms two oxides  $OF_2$  and  $O_2F_2$ . However, only  $OF_2$  is thermally stable at 298 K. These oxides

are essentially oxygen fluorides because of the higher electronegativity of fluorine than oxygen. Both are strong fluorinating agents.  $O_2F_2$  oxidises plutonium to  $PuF_6$  and the reaction is used in removing plutonium as  $PuF_6$  from spent nuclear fuel.

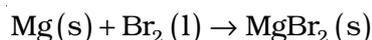
Chlorine, bromine and iodine form oxides in which the oxidation states of these halogens range from +1 to +7. A combination of kinetic and thermodynamic factors lead to the generally decreasing order of stability of oxides formed by halogens,  $I > Cl > Br$ . The higher oxides of halogens tend to be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

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

The bromine oxides,  $Br_2O$ ,  $BrO_2$ ,  $BrO_3$  are the least stable halogen oxides (middle row anomaly) and exist only at low temperatures. They are very powerful oxidising agents.

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

- (iii) *Reactivity towards metals:* Halogens react with metals to form metal halides. For example, bromine reacts with magnesium to give magnesium bromide.



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 lower oxidation state. For example,  $SnCl_4$ ,  $PbCl_4$ ,  $SbCl_5$  and  $UF_6$  are more covalent than  $SnCl_2$ ,  $PbCl_2$ ,  $SbCl_3$  and  $UF_4$  respectively.

- (iv) *Reactivity of halogens towards other halogens:* Halogens combine amongst themselves to form a number of compounds known as interhalogens of the types  $XX'$ ,  $XX_3'$ ,  $XX_5'$  and  $XX_7'$  where X is a larger size halogen and X' is smaller size halogen.

### Example 7.10

Fluorine exhibits only -1 oxidation state whereas other halogens exhibit +1, +3, +5 and +7 oxidation states also. Explain.

### Solution

Fluorine is the most electronegative element and cannot exhibit any positive oxidation state. Other halogens have *d* orbitals and therefore, can expand their octets and show +1, +3, +5 and +7 oxidation states also.

### Intext Questions

- 7.26** Considering the parameters such as bond dissociation enthalpy, electron gain enthalpy and hydration enthalpy, compare the oxidising power of  $F_2$  and  $Cl_2$ .
- 7.27** Give two examples to show the anomalous behaviour of fluorine.
- 7.28** Sea is the greatest source of some halogens. Comment.

## 7.19 Chlorine

Chlorine was discovered in 1774 by Scheele by the action of HCl on  $\text{MnO}_2$ . In 1810 Davy established its elementary nature and suggested the name chlorine on account of its colour (Greek, *chloros* = greenish yellow).

### Preparation

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

- (i) By heating manganese dioxide with concentrated hydrochloric acid.



However, a mixture of common salt and concentrated  $\text{H}_2\text{SO}_4$  is used in place of HCl.

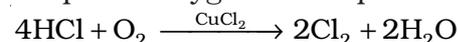


- (ii) By the action of HCl on potassium permanganate.



### Manufacture of chlorine

- (i) *Deacon's process*: By oxidation of hydrogen chloride gas by atmospheric oxygen in the presence of  $\text{CuCl}_2$  (catalyst) at 723 K.



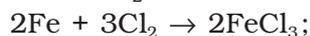
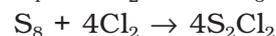
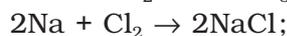
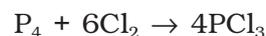
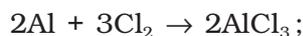
- (ii) *Electrolytic process*: Chlorine is obtained by the electrolysis of brine (concentrated NaCl solution). Chlorine is liberated at anode.

It is also obtained as a by-product in many chemical industries.

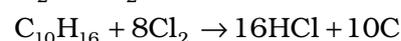
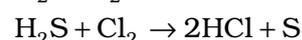
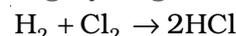
### Properties

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

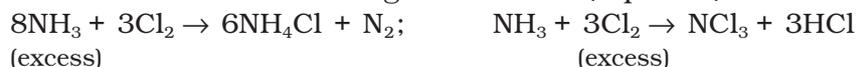
Chlorine reacts with a number of metals and non-metals to form chlorides.



It has 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 alkalis chlorine produces a mixture of chloride and hypochlorite but with hot and concentrated alkalis it gives chloride and chlorate.

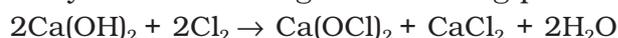


(cold and dilute)



(hot and conc.)

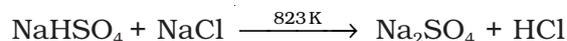
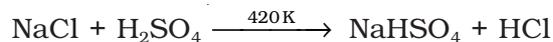
With dry slaked lime it gives bleaching powder.





### Preparation

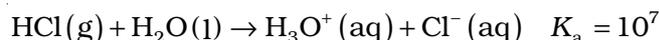
In laboratory, it is prepared by heating sodium chloride with concentrated sulphuric acid.



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

### Properties

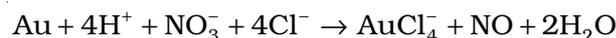
It is a colourless and pungent smelling gas. It is easily liquefied to a colourless liquid (b.p. 189 K) and freezes to a white crystalline solid (f.p. 159 K). It is extremely soluble in water and ionises as follows:



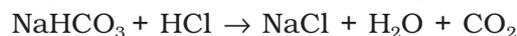
Its aqueous solution is called hydrochloric acid. High value of dissociation constant ( $K_a$ ) indicates that it is a strong acid in water. It reacts with  $\text{NH}_3$  and gives white fumes of  $\text{NH}_4\text{Cl}$ .



When three parts of concentrated 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.



Hydrochloric acid decomposes salts of weaker acids, e.g., carbonates, hydrogencarbonates, sulphites, etc.

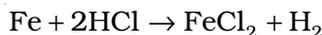


**Uses:** It is used (i) in the manufacture of chlorine,  $\text{NH}_4\text{Cl}$  and glucose (from corn starch), (ii) for extracting glue from bones and purifying bone black, (iii) in medicine and as a laboratory reagent.

When HCl reacts with finely powdered iron, it forms ferrous chloride and not ferric chloride. Why?

**Example 7.18**

Its reaction with iron produces  $\text{H}_2$ .



Liberation of hydrogen prevents the formation of ferric chloride.

**Solution**

## 7.21 Oxoacids of Halogens

Due to high electronegativity and small size, fluorine forms only one oxoacid, HOF known as fluoric (I) acid or hypofluorous acid. The other halogens form several oxoacids. Most of them cannot be isolated in pure state. They are stable only in aqueous solutions or in the form of their salts. The oxoacids of halogens are given in Table 7.10 and their structures are given in Fig. 7.8.

Table 7.10: Oxoacids of Halogens

| 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)   | –<br>–                     | HOClO<br>(chlorous acid)                | –<br>–                                 | –<br>–                               |
| Halic (V) acid<br>(Halic acid)      | –<br>–                     | 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) | –<br>–                     | HOClO <sub>3</sub><br>(perchloric acid) | HOBrO <sub>3</sub><br>(perbromic acid) | HOIO <sub>3</sub><br>(periodic acid) |

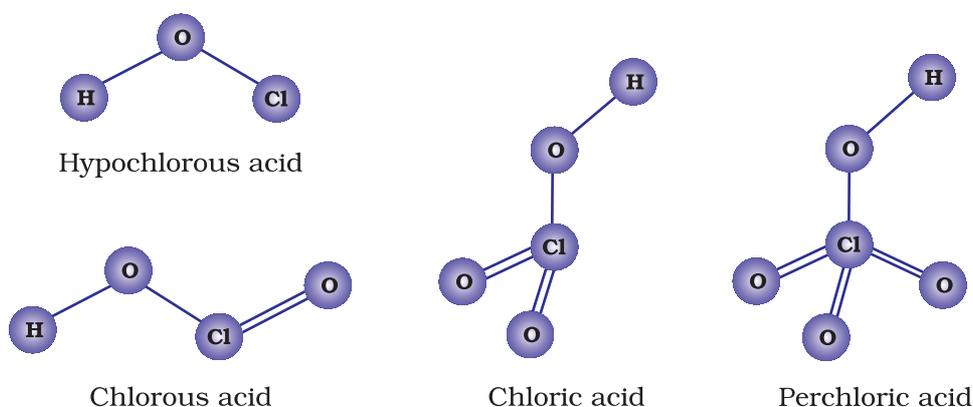


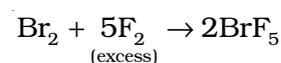
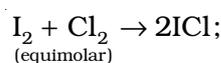
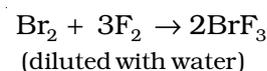
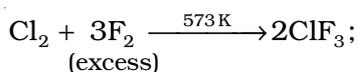
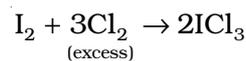
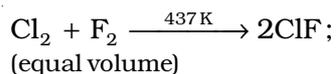
Fig. 7.8  
The structures of  
oxoacids of chlorine

## 7.22 Interhalogen Compounds

When two different halogens react with each other, interhalogen compounds are formed. They can be assigned general compositions as  $XX'$ ,  $XX'_3$ ,  $XX'_5$  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 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 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, For e.g.,



### Properties

Some properties of interhalogen compounds are given in Table 7.11.

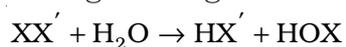
**Table 7.11: Some Properties of Interhalogen Compounds**

| Type             | Formula                       | Physical state and colour           | Structure              |
|------------------|-------------------------------|-------------------------------------|------------------------|
| XX' <sub>1</sub> | ClF                           | colourless gas                      | –                      |
|                  | BrF                           | pale brown gas                      | –                      |
|                  | IF <sup>a</sup>               | detected spectroscopically          | –                      |
|                  | BrCl <sup>b</sup>             | gas                                 | –                      |
|                  | ICl                           | ruby red solid (α-form)             | –                      |
|                  |                               | brown red solid (β-form)            | –                      |
|                  | I <sub>2</sub>                | black solid                         | –                      |
| XX' <sub>3</sub> | ClF <sub>3</sub>              | colourless gas                      | Bent T-shaped          |
|                  | BrF <sub>3</sub>              | yellow green liquid                 | Bent T-shaped          |
|                  | IF <sub>3</sub>               | yellow powder                       | Bent T-shaped (?)      |
|                  | ICl <sub>3</sub> <sup>c</sup> | orange solid                        | Bent T-shaped (?)      |
| XX' <sub>5</sub> | IF <sub>5</sub>               | colourless gas but solid below 77 K | Square pyramidal       |
|                  | BrF <sub>5</sub>              | colourless liquid                   | Square pyramidal       |
|                  | ClF <sub>5</sub>              | colourless liquid                   | Square pyramidal       |
| XX' <sub>7</sub> | IF <sub>7</sub>               | colourless gas                      | Pentagonal bipyramidal |

<sup>a</sup>Very unstable; <sup>b</sup>The pure solid is known at room temperature; <sup>c</sup>Dimerises as Cl-bridged dimer (I<sub>2</sub>Cl<sub>6</sub>)

These are all covalent molecules and are diamagnetic in nature. They are volatile solids or liquids at 298 K except 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.

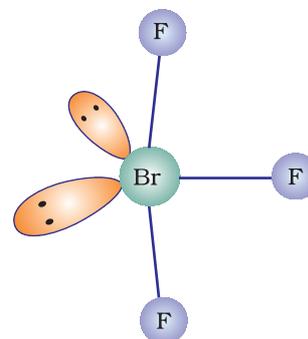
Their chemical reactions can be compared with the individual halogens. In general, interhalogen compounds are more reactive than halogens (except fluorine). This is because X–X' bond in interhalogens is weaker than X–X bond in halogens except F–F bond. All these undergo hydrolysis giving halide ion derived from the smaller halogen and a hypohalite (when XX'), halite (when XX'<sub>3</sub>), halate (when XX'<sub>5</sub>) and perchalate (when XX'<sub>7</sub>) anion derived from the larger halogen.



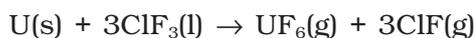
Their molecular structures are very interesting which can be explained on the basis of VSEPR theory (Example 7.19). The XX<sub>3</sub> compounds have the bent 'T' shape, XX<sub>5</sub> compounds square pyramidal and IF<sub>7</sub> has pentagonal bipyramidal structures (Table 7.11).

**Example 7.19** Discuss the molecular shape of  $\text{BrF}_3$  on the basis of VSEPR theory.

**Solution** The central atom Br has seven electrons in the valence shell. Three of these will form electron-pair bonds with three fluorine atoms leaving behind four electrons. Thus, there are three bond pairs and two lone pairs. According to VSEPR theory, these will occupy the corners of a trigonal bipyramid. The two lone pairs will occupy the equatorial positions to minimise lone pair-lone pair and the bond pair-lone pair repulsions which are greater than the bond pair-bond pair repulsions. In addition, the axial fluorine atoms will be bent towards the equatorial fluorine in order to minimise the lone-pair-lone pair repulsions. The shape would be that of a slightly bent 'T'.



**Uses:** These compounds can be used as non aqueous solvents. Interhalogen compounds are very useful fluorinating agents.  $\text{ClF}_3$  and  $\text{BrF}_3$  are used for the production of  $\text{UF}_6$  in the enrichment of  $^{235}\text{U}$ .



### Intext Question

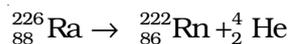
**7.31** Why is  $\text{ICl}$  more reactive than  $\text{I}_2$ ?

## 7.23 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.

### 7.23.1 Occurrence

All the noble gases except radon occur in the atmosphere. Their atmospheric abundance in dry air is ~ 1% by volume of which argon is the major constituent. Helium and sometimes neon are found in minerals of radioactive origin e.g., pitchblende, monazite, cleveite. The main commercial source of helium is natural gas. Xenon and radon are the rarest elements of the group. Radon is obtained as a decay product of  $^{226}\text{Ra}$ .



**Example 7.20** Why are the elements of Group 18 known as noble gases ?

**Solution** The elements present in Group 18 have their valence shell orbitals completely filled and, therefore, react with a few elements only under certain conditions. Therefore, they are now known as noble gases.

The important atomic and physical properties of the Group 18 elements along with their electronic configurations are given in Table 7.12. The trends in some of the atomic, physical and chemical properties of the group are discussed here.

**Table 7.12: Atomic and Physical Properties of Group 18 Elements**

| Property                                    | He                    | Ne                                  | Ar                                   | Kr   | Xe   | Rn*   |
|---|-----------------------|-------------------------------------|--------------------------------------|--|--|---|
| Atomic number                               | 2                     | 10                                  | 18                                   | 36   | 54   | 86  |
| Atomic mass/ g mol <sup>-1</sup>            | 4.00                  | 20.18                               | 39.95                                | 83.80  | 131.30   | 222.00  |
| Electronic configuration                    | 1s <sup>2</sup>       | [He]2s <sup>2</sup> 2p <sup>6</sup> | [Ne] 3s <sup>2</sup> 3p <sup>6</sup> | [Ar]3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>6</sup> | [Kr]4d <sup>10</sup> 5s <sup>2</sup> 5p <sup>6</sup> | [Xe]4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup> 6p <sup>6</sup> |
| Atomic radius/pm                            | 120                   | 160                                 | 190                                  | 200  | 220  | –   |
| Ionisation enthalpy /kJmol <sup>-1</sup>    | 2372                  | 2080                                | 1520                                 | 1351   | 1170   | 1037  |
| Electron gain enthalpy /kJmol <sup>-1</sup> | 48                    | 116                                 | 96                                   | 96   | 77   | 68  |
| Density (at STP)/gcm <sup>-3</sup>          | 1.8×10 <sup>-4</sup>  | 9.0×10 <sup>-4</sup>                | 1.8×10 <sup>-3</sup>                 | 3.7×10 <sup>-3</sup>                                 | 5.9×10 <sup>-3</sup>                                 | 9.7×10 <sup>-3</sup>  |
| Melting point/K                             | –                     | 24.6                                | 83.8                                 | 115.9  | 161.3  | 202   |
| Boiling point/K                             | 4.2                   | 27.1                                | 87.2                                 | 119.7  | 165.0  | 211   |
| Atmospheric content (% by volume)           | 5.24×10 <sup>-4</sup> | –                                   | 1.82×10 <sup>-3</sup>                | 0.934  | 1.14×10 <sup>-4</sup>                                | 8.7×10 <sup>-6</sup>  |

\* radioactive

**7.23.2 Electronic Configuration** All noble gases have general electronic configuration  $ns^2np^6$  except helium which has  $1s^2$  (Table 7.12). Many of the properties of noble gases including their inactive nature are ascribed to their closed shell structures.

**7.23.3 Ionisation Enthalpy** Due to stable electronic configuration these gases exhibit very high ionisation enthalpy. However, it decreases down the group with increase in atomic size.

**7.23.4 Atomic Radii** Atomic radii increase down the group with increase in atomic number.

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

#### **Physical Properties**

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

Noble gases have very low boiling points. Why?

**Example 7.21**

Noble gases being monoatomic have no interatomic forces except weak dispersion forces and therefore, they are liquefied at very low temperatures. Hence, they have low boiling points.

**Solution**

### Chemical Properties

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

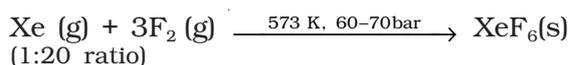
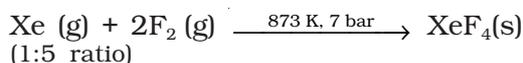
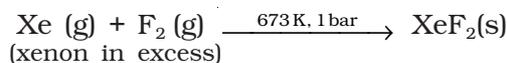
- (i) The noble gases except helium ( $1s^2$ ) have completely filled  $ns^2np^6$  electronic configuration in their valence shell.
- (ii) They have high ionisation enthalpy and more positive electron gain enthalpy.

The reactivity of noble gases has been investigated occasionally, ever since their discovery, but all attempts to force them to react to form the compounds, were unsuccessful for quite a few years. In March 1962, Neil Bartlett, then at the University of British Columbia, observed the reaction of a noble gas. First, he prepared a red compound which is formulated as  $O_2^+PtF_6^-$ . He, then realised that the first ionisation enthalpy of molecular oxygen ( $1175 \text{ kJ mol}^{-1}$ ) was almost identical with that of xenon ( $1170 \text{ kJ mol}^{-1}$ ). He made efforts to prepare same type of compound with Xe and was successful in preparing another red colour compound  $Xe^+PtF_6^-$  by mixing  $PtF_6$  and xenon. After this discovery, a number of xenon compounds mainly with most electronegative elements like fluorine and oxygen, have been synthesised.

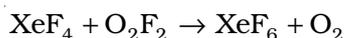
The compounds of krypton are fewer. Only the difluoride ( $KrF_2$ ) has been studied in detail. Compounds of radon have not been isolated but only identified (e.g.,  $RnF_2$ ) by radiotracer technique. No true compounds of Ar, Ne or He are yet known.

#### (a) Xenon-fluorine compounds

Xenon forms three binary fluorides,  $XeF_2$ ,  $XeF_4$  and  $XeF_6$  by the direct reaction of elements under appropriate experimental conditions.



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

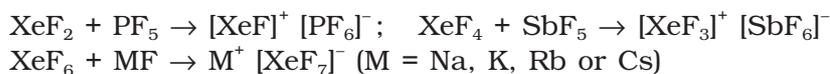


$XeF_2$ ,  $XeF_4$  and  $XeF_6$  are colourless crystalline solids and sublime readily at 298 K. They are powerful fluorinating agents. They are readily hydrolysed even by traces of water. For example,  $XeF_2$  is hydrolysed to give Xe, HF and  $O_2$ .



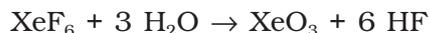
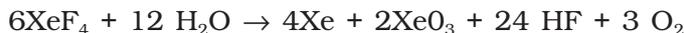
The structures of the three xenon fluorides can be deduced from VSEPR and these are shown in Fig. 7.9.  $XeF_2$  and  $XeF_4$  have linear and square planar structures respectively.  $XeF_6$  has seven electron pairs (6 bonding pairs and one lone pair) and would, thus, have a distorted octahedral structure as found experimentally in the gas phase.

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

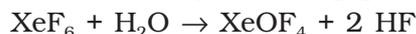


(b) Xenon-oxygen compounds

Hydrolysis of  $\text{XeF}_4$  and  $\text{XeF}_6$  with water gives  $\text{XeO}_3$ .



Partial hydrolysis of  $\text{XeF}_6$  gives oxyfluorides,  $\text{XeOF}_4$  and  $\text{XeO}_2\text{F}_2$ .



$\text{XeO}_3$  is a colourless explosive solid and has a pyramidal molecular structure (Fig. 7.9).  $\text{XeOF}_4$  is a colourless volatile liquid and has a square pyramidal molecular structure (Fig. 7.9).

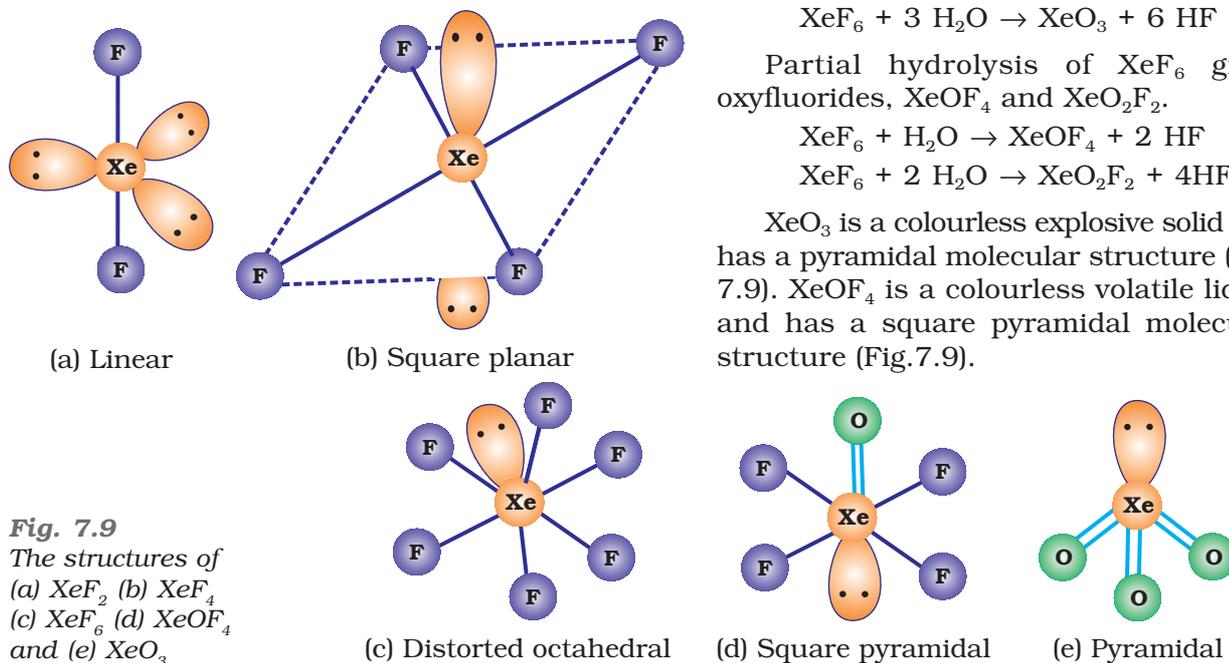


Fig. 7.9  
The structures of  
(a)  $\text{XeF}_2$  (b)  $\text{XeF}_4$   
(c)  $\text{XeF}_6$  (d)  $\text{XeOF}_4$   
and (e)  $\text{XeO}_3$

Does the hydrolysis of  $\text{XeF}_6$  lead to a redox reaction?

**Example 7.22**

No, the products of hydrolysis are  $\text{XeOF}_4$  and  $\text{XeO}_2\text{F}_2$  where the oxidation states of all the elements remain the same as it was in the reacting state.

**Solution**

**Uses:** 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 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 modern diving apparatus because of its very low solubility in blood.

Neon is used in discharge tubes and fluorescent bulbs for advertisement display purposes. Neon bulbs are used in botanical gardens and in green houses.

Argon is used mainly to provide an inert atmosphere in high temperature metallurgical processes (arc welding of metals or alloys) and for filling electric bulbs. It is also used in the laboratory for handling substances that are air-sensitive.

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

**Intext Questions**

7.32 Why is helium used in diving apparatus?

7.33 Balance the following equation:  $\text{XeF}_6 + \text{H}_2\text{O} \rightarrow \text{XeO}_2\text{F}_2 + \text{HF}$

7.34 Why has it been difficult to study the chemistry of radon?

## Summary

Groups 13 to 18 of the periodic table consist of **p-block elements** with their valence shell electronic configuration  $ns^2np^{1-6}$ . Groups 13 and 14 were dealt with in Class XI. In this Unit remaining groups of the p-block have been discussed.

**Group 15** consists of five elements namely, N, P, As, Sb and Bi which have general electronic configuration  $ns^2np^3$ . Nitrogen differs from other elements of this group due to small size, formation of  **$p\pi-p\pi$  multiple bonds** with itself and with highly electronegative atom like O or C and **non-availability of d orbitals** to expand its valence shell. Elements of group 15 show gradation in properties. They react with oxygen, hydrogen and halogens. They exhibit two important oxidation states, +3 and +5 but +3 oxidation is favoured by heavier elements due to 'inert pair effect'.

Dinitrogen can be prepared in laboratory as well as on industrial scale. It forms oxides in various oxidation states as  $N_2O$ , NO,  $N_2O_3$ ,  $NO_2$ ,  $N_2O_4$  and  $N_2O_5$ . These oxides have **resonating structures** and have multiple bonds. Ammonia can be prepared on large scale by **Haber's process**.  $HNO_3$  is an important industrial chemical. It is a strong monobasic acid and is a powerful oxidising agent. Metals and non-metals react with  $HNO_3$  under different conditions to give NO or  $NO_2$ .

Phosphorus exists as  $P_4$  in elemental form. It exists in several **allotropic forms**. It forms hydride,  $PH_3$  which is a highly poisonous gas. It forms two types of halides as  $PX_3$  and  $PX_5$ .  $PCl_3$  is prepared by the reaction of white phosphorus with dry chlorine while  $PCl_5$  is prepared by the reaction of phosphorus with  $SO_2Cl_2$ . Phosphorus forms a number of oxoacids. Depending upon the number of P-OH groups, their basicity varies. The oxoacids which have P-H bonds are good reducing agents.

**The Group 16** elements have general electronic configuration  $ns^2np^4$ . They show maximum oxidation state, +6. Gradation in physical and chemical properties is observed in the group 16 elements. In laboratory, dioxygen is prepared by heating  $KClO_3$  in presence of  $MnO_2$ . It forms a number of oxides with metals. Allotropic form of oxygen is  $O_3$  which is a highly oxidising agent. Sulphur forms a number of allotropes. Of these,  $\alpha$ - and  $\beta$ - forms of sulphur are the most important. Sulphur combines with oxygen to give oxides such as  $SO_2$  and  $SO_3$ .  $SO_2$  is prepared by the direct union of sulphur with oxygen.  $SO_2$  is used in the manufacture of  $H_2SO_4$ . Sulphur forms a number of oxoacids. Amongst them, the most important is  $H_2SO_4$ . It is prepared by **contact process**. It is a dehydrating and oxidising agent. It is used in the manufacture of several compounds.

**Group 17** of the periodic table consists of the following elements F, Cl, Br, I and At. These elements are extremely reactive and as such they are found in the combined state only. The common oxidation state of these elements is -1. However, highest oxidation state can be +7. They show regular gradation in physical and chemical properties. They form oxides, hydrogen halides, interhalogen compounds and oxoacids. Chlorine is conveniently obtained by the reaction of HCl with  $KMnO_4$ . HCl is prepared by heating NaCl with concentrated  $H_2SO_4$ . Halogens combine with one another to form **interhalogen compounds** of the type  $XX'_n$  ( $n = 1, 3, 5, 7$ ) where  $X'$  is lighter than X. A number of oxoacids of halogens are known. In the structures of these oxoacids, halogen is the central atom which is bonded in each case with one OH bond as X-OH. In some cases X = O bonds are also found.

**Group 18** of the periodic table consists of **noble gases**. They have  $ns^2np^6$  valence shell electronic configuration except He which has  $1s^2$ . All the gases except Rn occur in atmosphere. Rn is obtained as the decay product of  $^{226}Ra$ .

Due to complete octet of outermost shell, they have less tendency to form compounds. The best characterised compounds are those of xenon with fluorine and oxygen only under certain conditions. These gases have several uses. Argon is used to provide inert atmosphere, helium is used in filling balloons for meteorological observations, neon is used in discharge tubes and fluorescent bulbs.

## Exercises

- 7.1 Discuss the general characteristics of Group 15 elements with reference to their electronic configuration, oxidation state, atomic size, ionisation enthalpy and electronegativity.
- 7.2 Why does the reactivity of nitrogen differ from phosphorus?
- 7.3 Discuss the trends in chemical reactivity of group 15 elements.
- 7.4 Why does  $\text{NH}_3$  form hydrogen bond but  $\text{PH}_3$  does not?
- 7.5 How is nitrogen prepared in the laboratory? Write the chemical equations of the reactions involved.
- 7.6 How is ammonia manufactured industrially?
- 7.7 Illustrate how copper metal can give different products on reaction with  $\text{HNO}_3$ .
- 7.8 Give the resonating structures of  $\text{NO}_2$  and  $\text{N}_2\text{O}_5$ .
- 7.9 The HNH angle value is higher than HPH, HAsH and HSbH angles. Why? [Hint: Can be explained on the basis of  $sp^3$  hybridisation in  $\text{NH}_3$  and only  $s-p$  bonding between hydrogen and other elements of the group].
- 7.10 Why does  $\text{R}_3\text{P} = \text{O}$  exist but  $\text{R}_3\text{N} = \text{O}$  does not (R = alkyl group)?
- 7.11 Explain why  $\text{NH}_3$  is basic while  $\text{BiH}_3$  is only feebly basic.
- 7.12 Nitrogen exists as diatomic molecule and phosphorus as  $\text{P}_4$ . Why?
- 7.13 Write main differences between the properties of white phosphorus and red phosphorus.
- 7.14 Why does nitrogen show catenation properties less than phosphorus?
- 7.15 Give the disproportionation reaction of  $\text{H}_3\text{PO}_3$ .
- 7.16 Can  $\text{PCl}_5$  act as an oxidising as well as a reducing agent? Justify.
- 7.17 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.
- 7.18 Why is dioxygen a gas but sulphur a solid?
- 7.19 Knowing the electron gain enthalpy values for  $\text{O} \rightarrow \text{O}^-$  and  $\text{O} \rightarrow \text{O}^{2-}$  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).
- 7.20 Which aerosols deplete ozone?
- 7.21 Describe the manufacture of  $\text{H}_2\text{SO}_4$  by contact process?
- 7.22 How is  $\text{SO}_2$  an air pollutant?
- 7.23 Why are halogens strong oxidising agents?
- 7.24 Explain why fluorine forms only one oxoacid, HOF.
- 7.25 Explain why in spite of nearly the same electronegativity, nitrogen forms hydrogen bonding while chlorine does not.
- 7.26 Write two uses of  $\text{ClO}_2$ .
- 7.27 Why are halogens coloured?
- 7.28 Write the reactions of  $\text{F}_2$  and  $\text{Cl}_2$  with water.
- 7.29 How can you prepare  $\text{Cl}_2$  from  $\text{HCl}$  and  $\text{HCl}$  from  $\text{Cl}_2$ ? Write reactions only.
- 7.30 What inspired N. Bartlett for carrying out reaction between Xe and  $\text{PtF}_6$ ?
- 7.31 What are the oxidation states of phosphorus in the following:  
(i)  $\text{H}_3\text{PO}_3$       (ii)  $\text{PCl}_3$       (iii)  $\text{Ca}_3\text{P}_2$       (iv)  $\text{Na}_3\text{PO}_4$       (v)  $\text{POF}_3$ ?

- 7.32** Write balanced equations for the following:  
 (i) NaCl is heated with sulphuric acid in the presence of MnO<sub>2</sub>.  
 (ii) Chlorine gas is passed into a solution of NaI in water.
- 7.33** How are xenon fluorides XeF<sub>2</sub>, XeF<sub>4</sub> and XeF<sub>6</sub> obtained?
- 7.34** With what neutral molecule is ClO<sup>-</sup> isoelectronic? Is that molecule a Lewis base?
- 7.35** How are XeO<sub>3</sub> and XeOF<sub>4</sub> prepared?
- 7.36** Arrange the following in the order of property indicated for each set:  
 (i) F<sub>2</sub>, Cl<sub>2</sub>, Br<sub>2</sub>, I<sub>2</sub> - increasing bond dissociation enthalpy.  
 (ii) HF, HCl, HBr, HI - increasing acid strength.  
 (iii) NH<sub>3</sub>, PH<sub>3</sub>, AsH<sub>3</sub>, SbH<sub>3</sub>, BiH<sub>3</sub> - increasing base strength.
- 7.37** Which one of the following does not exist?  
 (i) XeOF<sub>4</sub>                      (ii) NeF<sub>2</sub>                      (iii) XeF<sub>2</sub>                      (iv) XeF<sub>6</sub>
- 7.38** Give the formula and describe the structure of a noble gas species which is isostructural with:  
 (i) ICl<sub>4</sub><sup>-</sup>                      (ii) IBr<sub>2</sub><sup>-</sup>                      (iii) BrO<sub>3</sub><sup>-</sup>
- 7.39** Why do noble gases have comparatively large atomic sizes?
- 7.40** List the uses of neon and argon gases.

#### Answers to Some Intext Questions

- 7.1** Higher the positive oxidation state of central atom, more will be its polarising power which, in turn, increases the covalent character of bond formed between the central atom and the other atom.
- 7.2** Because BiH<sub>3</sub> is the least stable among the hydrides of Group 15.
- 7.3** Because of strong pπ-pπ overlap resulting into the triple bond, N≡N.
- 7.6** From the structure of N<sub>2</sub>O<sub>5</sub> it is evident that covalence of nitrogen is four.
- 7.7** Both are sp<sup>3</sup> hybridised. In PH<sub>4</sub><sup>+</sup> all the four orbitals are bonded whereas in PH<sub>3</sub> there is a lone pair of electrons on P, which is responsible for lone pair-bond pair repulsion in PH<sub>3</sub> reducing the bond angle to less than 109° 28'.
- 7.10** PCl<sub>5</sub> + D<sub>2</sub>O → POCl<sub>3</sub> + 2DCl
- 7.11** Three P-OH groups are present in the molecule of H<sub>3</sub>PO<sub>4</sub>. Therefore, its basicity is three.
- 7.15** Because of small size and high electronegativity of oxygen, molecules of water are highly associated through hydrogen bonding resulting in its liquid state.
- 7.21** Both the S-O bonds are covalent and have equal strength due to resonating structures.
- 7.25** H<sub>2</sub>SO<sub>4</sub> is a very strong acid in water largely because of its first ionisation to H<sub>3</sub>O<sup>+</sup> and HSO<sub>4</sub><sup>-</sup>. The ionisation of HSO<sub>4</sub><sup>-</sup> to H<sub>3</sub>O<sup>+</sup> and SO<sub>4</sub><sup>2-</sup> is very very small. That is why K<sub>a2</sub> ≪ K<sub>a1</sub>.
- 7.31** In general, interhalogen compounds are more reactive than halogens due to weaker X-X<sup>1</sup> bonding than X-X bond. Thus, ICl is more reactive than I<sub>2</sub>.
- 7.34** Radon is radioactive with very short half-life which makes the study of chemistry of radon difficult.