MODULE-6

Chemistry of Elements





p-BLOCK ELEMENTS AND THEIR COMPOUNDS - II

You have already studied the chemistry of the elements of Groups 13, 14 and 15. In this lesson we shall deal with the chemistry of the elements of Groups 16, 17 and 18.

Objectives

After reading this lesson you will be able to:

- classify oxides into acidic, basic and amphoteric types;
- describe the manufacture of sulphuric acid;
- recall the preparation, properties and uses of ozone;
- recall the characteristics of hydrogen halides (HF, HCl);
- list the oxides and oxoacids of chlorine;
- compare the acidic behaviour of oxoacids of chlorine;
- write the general molecular formulae of interhalogen compounds;
- discuss the structures of interhalogen compounds;
- list a few chloro fluoro carbons and explain their uses and their effect on environment;
- explain the unreactive nature of noble gases;
- recall the preparation of xenon fluorides and oxides, and
- illustrate the structures of XeF_2 , XeF_4 , XeF_6 , XeO_3 and XeO_4 .

22.1 Oxygen and Sulphur

Oxygen and sulphur are the first two members of the 16th group of the periodic table.

In this section you will learn about some compounds of oxygen and sulphur including environmentally important ozone and industrially important sulphuric acid.

22.1.1. Classification of Oxides

The binary compounds of oxygen with other elements (metals or non-metals) are called oxides. An understanding of the nature of an oxide provides a clue to the nature of the element which forms the oxide. Depending upon the acid-base behaviour of the oxides, they can be classified into the following categories.

(1) Acidic oxides

(2) Basic oxides

(3) Amphoteric oxides

(4) Neutral oxides

(1) Acidic Oxides : Acidic oxides are generally formed by non-metallic elements and some metals in higher oxidation states. Examples of some acidic oxides are CO_2 , SO_2 , N_2O_5 , P_4O_{10} , Cl_2O_7 , Mn_2O_7 , etc. These oxides combine with water to form acids whereas with alkalies they form salt and water.

 $\begin{array}{rclcrcl} \mathrm{SO}_2 & + & \mathrm{H_2O} & \longrightarrow & \mathrm{H_2SO_3} \\ \\ \mathrm{SO}_2 & + & 2\mathrm{NaOH} & \longrightarrow & \mathrm{Na_2SO_3} & + & \mathrm{H_2O} \end{array}$

However, certain acidic oxides do not form acids on reacting with water. But they react with alkalies to form salt and water, e.g., SiO₂

 $SiO_2 + 2 NaOH \longrightarrow Na_2SiO_3 + H_2O$ Sodium silicate

(2) **Basic oxides :** Metals combine with oxygen to form basic oxides. The basic oxides react with acids to form salt and water.

FeO	+	H_2SO_4	\longrightarrow	FeSO ₄ +	H_2)
CuO	+	2HNO ₃	\longrightarrow	$Cu(NO_3)_2$	+	H ₂ C

The oxides of the metals of Groups 1 and 2 react with water to form hydroxides known as **alkalies**.

 $Na_2O + H_2O \longrightarrow 2NaOH$

(3) Amphoteric oxides : Almost all metallic oxides are basic oxides. But some metallic oxides show the characteristics of both acidic as well as basic oxides, i.e., they react with both acids as well as bases to form salt and water. Such oxides are called *amphoteric oxides*. The oxides of zinc, aluminium, lead and tin are amphoteric in nature.

$$\begin{array}{rclcrcl} {\rm ZnO} &+& {\rm H_2SO_4} &\longrightarrow & {\rm ZnSO_4} &+& {\rm H_2O} \\ {\rm ZnO} &+& {\rm 2NaOH} &\longrightarrow & {\rm Na_2\,ZnO_2} &+& {\rm H_2O} \\ && & & & \\ {\rm Sodium\,zincate} \\ {\rm Al_2O_3} &+& {\rm 6HCl} &\longrightarrow & {\rm 2AlCl_3} &+& {\rm 3H_2O} \\ {\rm Al_2O_3} &+& {\rm 2NaOH} &\longrightarrow & {\rm 2NaAlO_2} &+& {\rm H_2O} \\ && & & & \\ {\rm Sodium\,aluminate} \end{array}$$

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(4) Neutral oxides : These oxides are neither acidic nor basic. Examples are carbon monoxide, (CO), nitric oxide (NO), nitrous oxide (N_2O) , etc.

Intext Questions 22.1

- 1. Give one example each of basic oxide, acidic oxide and amphoteric oxide.
- 2. Classify the following oxides into acidic, basic or amphoteric oxides : K₂O, SiO₂, SO₂, FeO, Al₂O₃, ZnO, CrO₃.
- 3. Give chemical equations to illustrate the amphoteric behaviour of ZnO.
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- 4. Name the compound formed when the oxide of an element of Group 1 or 2 reacts with acid?

22.2 Ozone

Ozone is an allotrope of oxygen. You must have learnt through the media that ozone layer depletion in the upper atmosphere is causing a great environmental concern. We will now study the preparation, properties, importance and uses of ozone.

Ozone is formed around high voltage electrical installations. Traces of ozone are formed in forests by decay of organic matter. Ozone is prepared industrially by Siemen's ozonizer.

Siemens ozonizer : In this apparatus metal electrodes are used to produce an electric field. Two coaxial glass tubes are fused together at one end. The outer tube has an inlet for oxygen or air and an outlet for ozone (with oxygen or air). The inner side of the inner tube and the outer side of the outer tube are coated with tinfoil (T). These are connected to the terminals of an induction coil or high voltage transformer.



Fig. 22.1 : Siemen's Ozonizer

Pure, dry and cold oxygen or air is passed through the inlet in a slow current. Electrical energy is absorbed and about 5 to 10 percent of oxygen is converted into ozone.

All rubber and cork fittings are avoided because of the corrosive action of ozone on these materials.

Structure of Ozone : Ozone forms a V-shaped molecule. The central O atom uses sp^2 hybrid orbitals for bonding. The structure of ozone can be explained as a resonance hybrid of the following two structures, (oxygen – oxygen bond length 128 pm and bond angle 117°)



Properties of Ozone

- (a) **Physical :** Ozone is a pale blue gas which turns into blue liquid at 161K. At 80K it freezes to a violet black solid. It is ten times as soluble in water as oxygen.
- (b) **Chemical :** The chief characteristic of ozone is that it is unstable and that it gives energy loaded nascent oxygen. Its reactions are closely paralleled to the reactions of hydrogen peroxide.
- 1. *Catalytic decomposition :* Ozone in aqueous solution decomposes on standing. Above 373K ozone decomposes very rapidly. Even at ordinary temperature it decomposes in the presence of chlorine, bromine, nitrogen pentoxide and other acidic oxides and oxides of transition metals.

$$2O_3 \rightarrow 3O_2$$
.

2. *Oxidizing properties* : In the presence of reducing agents ozone furnishes active atom of oxygen according to the equation.

$$O_3 \rightarrow O_2 + O$$

In most of the reactions, oxygen gas is liberated as the reduction product from ozone.

(i) It oxidizes black lead sulphide to white lead sulphate

 $4O_3 + PbS \rightarrow PbSO_4 + 4O_2$

(ii) Ozone oxidizes acidified ferrous sulphate to ferric sulphate

$$O_3 + 2FeSO_4 + H_2SO_4 \rightarrow Fe_2(SO_4)_3 + H_2O + O_2$$

(iii) Ozone oxidizes moist sulphur to sulphuric acid and phosphorus to phosphoric acid.

$$3O_3 + S + H_2O \rightarrow H_2SO_4 + 3O_2$$

$$5O_3 + 2P + 3H_2O \rightarrow 2H_3PO_4 + 5O_4$$

(iv) Ozone tails mercury. Normally mercury does not stick to glass but if exposed to ozone it loses its convex meniscus and leaves a 'tail' or trail of minute droplets on a glass surface. This is supposed to be due to the formation of stray molecules of mercurous oxide which affect the surface only.

 $O_3 + 2Hg \rightarrow Hg_2O + O_2$

The 'tailing' effect can be removed by washing with dilute acid.

(v) Ozone oxidizes stannous chloride to stannic chloride. Note that no oxygen is produced in this reaction.

$$O_3 + 3SnCl_2 + 6HCl \rightarrow 3SnCl_4 + 3H_2O$$

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3. *Ozonides* : All unsaturated organic compounds combine with ozone to form unstable compounds called ozonides, e.g.



The ozonides are hydrolysed by water to give aldehydes or ketones or both.

$$\begin{array}{ccc} CH_2 & & O \\ | & & \\ O & & \\ | & & \\ | & \\ CH_2 & & O \end{array} + H_2O \rightarrow 2HCHO + H_2O_2$$

This technique is called *ozonolysis* and is widely used to locate the position of double bond in organic compounds.

Uses of Ozone

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Some of its applications are given below :

- 1. *Water purification :* Small ozone-air plants function as part of the water purification set up. Ozone is a powerful germicide and it can purify a water spray effectively; it does not produce the unwanted by-products that other sterilizing agents do.
- **2.** *Air purification* : Ozone is also used to purify air in tunnels, wells and crowded subways and cinema halls.
- **3.** *Refining oils*: Vegetable oil and ghee go rancid when stored for a long time. This is caused by bacterial growth in the small water content present in them. If ozone is bubbled through oil, all such growing organisms are destroyed and we get purified oil.
- 4. *Dry bleach* : Ozone is also used to bleach waxes, flour, sugar and starch. Hydrogen peroxide, which produces water and other agents which act only in solution, cannot be used in these cases.
- 5. *In Industry and in the Laboratory* : It is widely used in certain organic preparation. Its use in ozonolyses has already been mentioned.

Intext Questions 22.2

- 1. What are ozonides? What happens when an ozonide is hydrolysed?
- 2. Write the reactions which occur when ozone reacts with (i) ferrous sulphate (ii) stannous chloride

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- 3. Which is more soluble in water, oxygen or ozone?
 -
- 4. Draw the structure of ozone molecule, O_3 .
- 5. What is meant by "tailing of mercury"? How is it removed?

22.3 Sulphuric Acid

The most important compound of sulphur is sulphuric acid. Sulphuric acid or the 'oil of Vitriol' was known to the alchemists and their predecessors. Before the coming of Chamber process in the last century, it was obtained by heating hydrated sulphates.

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Manufacture : The two main processes used for the manufacture of sulphuric acid are (1) Lead Chamber process and (2) the Contact process. Nowadays sulphuric acid is mostly manufactured by Contact process.

Manufacture of sulphuric acid by Contact Process involves the following steps:

(i) Sulphur dioxide gas is produced by burning sulphur in air or by roasting of pyrites.

 $S + O_2 \longrightarrow SO_2$ $4FeS_2 + 11O_2 \longrightarrow 2Fe_2O_3 + 8SO_2$

- (ii) Sulphur dioxide produced is then freed from dust and other impurities such as arsenic compounds.
- (iii) The purified sulphur dioxide in then oxidized by atmospheric oxygen to sulphur trioxide in the presence of a catalyst, vanadium (V) oxide, V_2O_5 heated to 720K.

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

The plant is operated at a pressure of 2 atmosphere and temperature of 720K.

(iv) The sulphur trioxide gas in then absorbed in conc. H_2SO_4 to form $oleum(H_2S_2O_7)$. If SO₃ is directly dissolved in water, a highly corrosive mist of sulphuric acid is formed.

 $SO_3 + H_2SO_4 \longrightarrow H_2S_2O_7$

(v) Oleum is then diluted with water to obtain sulphuric acid of desired strength.

 $H_2S_2O_7 + H_2O \longrightarrow 2H_2SO_4$

The sulphuric acid obtained from the contact process is about 96-98% pure.

Properties of Sulphuric acid

(i) **Physical properties :** Pure sulphuric acid is a thick colourless oily liquid. Its melting point is 283.5K. Concentrated sulphuric acid dissolves in water with the liberation of a

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large amount of heat. While preparing dilute H_2SO_4 , water must not be added to conc. H_2SO_4 . Dilute sulphuric acid is prepared by adding conc. H_2SO_4 slowly and with constant stirring to water. If water is added to the acid, the heat produced is so large that it could throw out drops of sulphuric acid and burn you.

Chemical properties : The most important properties of sulphuric acid are its oxidizing and dehydrating properties.

(i) **Oxidizing properties :** Hot concentrated sulphuric acid acts as an oxidizing agent and oxidizes metals, non-metals and compounds.

Oxidation of metals.

 $\begin{array}{rcl} Cu + 2H_2SO_4 & \longrightarrow & CuSO_4 + 2H_2O + SO_2 \\ \\ Zn + 2H_2SO_4 & \longrightarrow & ZnSO_4 + 2H_2 \end{array}$

Oxidation of non-metals

 $C + 2H_2SO_4 \longrightarrow CO_2 + 2SO_2 + 2H_2O$ $S + 2H_2SO_4 \longrightarrow 3SO_2 + 2H_2O$

Oxidation of compounds

 $2HBr + H_2SO_4 \longrightarrow 2H_2O + SO_2 + Br_2$ $8HI + H_2SO_4 \longrightarrow 4H_2O + H_2S + 4I_2$ $3H_2S + H_2SO_4 \longrightarrow 4S + 4H_2O$

Dehydrating properties : Conc. H_2SO_4 is a strong dehydrating agent. It removes water of crystallization from copper sulphate (which is blue in colour) and turns it to white colour.

It also removes water from carbohydrates leaving behind, black mass of carbon.

 $C_{12}H_{22}O_{11} \xrightarrow{\text{conc. H}_2SO_4} 12C + 11H_2O$

Uses of Sulphuric Acid

Sulphuric acid is known as the king of chemicals. It is practically used in every industry. It is used in the manufacture of fertilizers, paints and pigments, detergents, plastics and fibres, etc.

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Intext Questions 22.3

1. Write a reaction to show the

(i) oxidizing property of sulphuric acid

(ii) dehydrating property of sulphuric acid

- 2. In the manufacture of sulphuric acid by Contact process, SO_3 is dissolved in conc. H_2SO_4 and not in water. Why?
 -
- 3. Write the reaction that takes place in the presence of a catalyst in the contact process.

22.4 Fluorine and Chlorine

Fluorine and chlorine are the first two members of Group17. Fluorine is the most electronegative element. In this section we shall briefly learn about fluorine and chlorine and study in some detail about the hydrogen halides, oxides and oxoacids of chlorine and interhalogen compounds.

Fluorine is extremely difficult to prepare owing to its highly reactive nature. It is the strongest chemical oxidizing agent hence cannot be prepared by oxidation of fluoride ions. It is prepared by the electrolysis of potassium hydrogen fluoride (KHF₂) in anhydrous hydrogen fluoride. Hydrogen fluoride undergoes electrolytic dissociation.

$$2HF \rightarrow F_2 + H_2$$

The fluorine obtained is contaminated with hydrogen fluoride which may be removed by passing the gas over solid NaF.

Fluorine is a pale yellow gas which fumes in air.

$$2F_2 + 2H_2O \rightarrow 4HF + O_2.$$

Fluorine is highly reactive. It combines with various metals and non-metals to form fluorides. With hydrogen halides it acts as an oxidizing agent, e.g.

 $2HX + F_2 \rightarrow 2HF + X_2$ (X = Cl, Br or I)

Fluorine is widely used in the preparation of fluorinated hydrocarbons which in turn find various uses in industry.

Chlorine is usually prepared by the oxidation of chlorides by strong oxidizing agents, such as MnO_2 , $KMnO_4$.

$$MnO_2 + 2Cl^- + 4H^+ \rightarrow Mn^{2+} + 2H_2O + Cl_2$$

$$2MnO_4^- + 16H^+ + 10Cl^- \rightarrow 2Mn^{2+} + 5Cl_2 + 8H_2O$$

On a large scale chlorine is obtained as a by product in the electrolysis of sodium chloride.

Chlorine is a greenish yellow gas and can be liquified by pressure alone at room temperature, It is quite reactive and forms chlorides of metals and nonmetals when reacted with them. It also oxidizes ammonia to nitrogen

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

Large quantities of chlorine are used in bleaching industry and in the manufacture of plastics, synthetic rubbers, antiseptics and insecticides.

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22.4.1 Hydrogen Halides and Hydrohalic Acids

The hydrogen halides under consideration are HF, HCl, HBr and HI. The bond distance H-X increases with the size of halogen atom. The bond also becomes more covalent and less ionic. Since the bond length increases, the hydrogen halide in aqueous solution loses hydrogen ion more easily with increasing size of halogen, and the acid strength increases in the order HF < HCl < HBr < Hl

The aqueous solutions of hydrogen halides are, in general, known as hydrohalic acids or simply halogen acids (hydrofluoric, hydrochloric hydrobromic, and hydroiodic acids)

Preparation of Hydrogen Halides

Industrially HF is made by heating CaF₂ with strong H₂SO₄.

 $\label{eq:cap_constraint} \text{CaF}_{2} + \text{H}_2\text{SO}_4 \longrightarrow \quad \text{CaSO}_4 + 2\text{HF}$

Hydrogen chloride is made by heating a mixture of NaCl and conc. H_2SO_4 at 423 K.

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

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

High purity HCl is made by the direct combination of the elements $(H_2 \text{ and } Cl_2)$

 $H_2 + Cl_2 \longrightarrow 2HCl$

Phosphoric acid is used to make HI

 $H_3PO_4 + Nal \longrightarrow Hl + NaH_2PO_4$

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

 $2P + 3Br_{2} \longrightarrow 2PBr_{3}$ $PBr_{3} + 6H_{2}O \longrightarrow 6HBr + 2H_{3}PO_{3}$ $2P + 3I_{2} \longrightarrow 2PI_{3}$ $2PI_{3} + 6H_{2}O \longrightarrow 6HI + 2H_{3}PO_{3}$

Properties of the Halogen Halides

- HF is a liquid at room temperature (b.p. 293 K), whereas HCl, HBr and HI are gases.
- The boiling point of HF is unexpectedly high as compared to HCl (189K), HBr (206K) and HI (238K). This is due to the formation of hydrogen bonds between the F atom of one molecule and the H atom of another molecule (Fig. 22.2).



Fig. 22.2 : Hydrogen bonded chain in HF

In the gaseous state, the hydrogen halides are essentially covalent. In the aqueous solutions they ionize to form ions but HF ionizes to a very small extent

$$HF + H_2O \longrightarrow H_3O^+ + F^-$$

The bond dissociation energy of the hydrogen halides follow the order HF>HCl>HBr>HI.

The stability of hydrogen halides to thermal decomposition therefore decreases in the order HF > HCl > HBr > HI. The acid strength of the acids increases in the order HF < HCl < HBr < HI. The aqueous solution known as hydrofluoric acid, hydrochloric acid, hydrobromic acid and hydroiodic acid possess the usual property of acids, e.g. they react with bases to form salts and water and with metals to form salts and hydrogen.

Uses of Hydrogen Halides

Hydrogen fluoride is used to prepare certain fluorides mainly fluorocarbons or freons. It is also used in etching glass and in removing sand from casting. Hydrogen chloride is primarily used for preparing chlorides. Large quantities of hydrochloric acid are used in the manufacture of aniline dyes and for cleaning iron before galvanization. Hydrogen bromide and hydrogen iodide are used to prepare bromide and iodide salts. Hydrogen iodide is also used as a reducing agent in organic chemistry.

22.4.2 Oxides and Oxoacids of Halogens

There are several compounds containing halogen and oxygen. Oxygen is less electronegative than fluorine, hence the compounds of oxygen with fluorine are known as oxygen fluorides (e.g. OF_2). Other halogens are less electronegative than oxygen. Thus they are known as halogen oxides. Only the oxides of chlorine are important and they are described here.

Oxides of chlorine The main oxides are listed below :

Chlorine monoxide, Cl₂O

Chlorine dioxide, ClO₂

Chlorine hexoxide, Cl₂O₆

Chlorine heptoxide, Cl₂O₇

Chlorine monoxide, Cl_2O , is prepared by passing chlorine over freshly prepared mercury (II) oxide

 $2 \text{ Cl}_2 + 2 \text{ HgO} \longrightarrow \text{Cl}_2\text{O} + \text{HgO. HgCl}_2$

It is a pale yellow gas which decomposes violently on heating and dissolves in water forming hypochlorous acid. $Cl_2O + H_2O \longrightarrow 2HOCl$

It is a powerful oxidizing agent.

Chlorine dioxide, ClO_2 , is prepared by the action of concentrated sulphuric acid on potassium chlorate

 $\begin{array}{c} \mathrm{KClO}_3 + \mathrm{H}_2\mathrm{SO}_4 & \longrightarrow & \mathrm{HClO}_3 + \mathrm{KHSO}_4.\\ & & \mathbf{chloric\ acid} \\ 3\mathrm{HClO}_3 & \longrightarrow & \mathrm{HClO}_4 + 2\mathrm{ClO}_2 + \mathrm{H}_2\mathrm{O}\\ & & \mathbf{perchloric\ acid} \end{array}$

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It is an orange gas and explosive in nature.

Chlorine hexoxide, Cl_2O_6 , is prepared by the action of ozone on chlorine at low temperature. It is a red liquid and dissolves in alkalies producing chlorate and perchlorate

$$Cl_{2}O_{6} + 2OH^{-} \longrightarrow ClO_{3}^{-} + ClO_{4}^{-} + H_{2}O$$

Chlorine heptoxide, Cl_2O_7 , is prepared by the action of phosphorus pentoxide on anhydrous perchloric acid at 263 K.

 $P_4O_{10} + 4HClO_4 \longrightarrow 4 HPO_3 + 2Cl_2O_7$

It is a colourless oil which explodes on heating or striking.

The structures of chlorine oxides are as follows :



Oxoacids of chlorine

Chlorine forms four oxoacids, HOCl, HOClO, HOClO, and HOClO,

Hypochlorous acid, HOCl is known only in solution - It is prepared by shaking chlorine water.

 $Cl_2 + H_2O \longrightarrow HOCl + HCl$

Its salt NaOCl is used as a bleaching agent.

Chlorous acid, HOClO is also known in solution, certain chlorite salts of alkali and alkaline earth metals are known in solid state, e.g., $NaClO_2$, $3H_2O$. The acid is prepared by the action of barium chlorite with sulphuric acid.

Ba $(ClO_2)_2 + H_2SO_4 \longrightarrow 2HClO_2 + BaSO_4$

barium chlorite

Chloric acid, HOClO₂ is prepared by the action of barium chlorate with sulphuric acid.

 $Ba (ClO_3)_2 + H_2SO_4 \longrightarrow HClO_2 + BaSO_4$

barium chlorate

Perchloric acid, HOClO₃, is prepared by distilling potassium perchlorate with concentrated sulphuric acid under reduced pressure

$$2\text{KClO}_4 + \text{H}_2\text{SO}_4 \longrightarrow 2\text{HClO}_4 + \text{K}_2\text{SO}_4$$

potassium perchlorate

It is a colourless oily liquid and combines vigonously with water forming hydronium perchlorate (H_3O^+ ClO₄⁻). It is one of the strong acids. It is also an oxidizing agent.

The oxoacids of chlorine are listed in the following table showing their structures.



Table 22.1 : Oxoacids of chlorine

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The acid strength of the oxoacids of chlorine increases as the number of O-atoms present in the acid increases. It is because oxygen is more electronegative then chlorine. As the number of O atoms bonded to the Cl atom increases, more electrons will be pulled away more strongly from the O–H bond. As a result the O–H bond will be weakened. Thus $HOCIO_3$ require the least energy to break the O–H bond and form H⁺. Thus, HOCl is a very weak acid whereas $HOCIO_3$ is the strongest acid, thus the acid strength increases in the order.

 $HOCl < HOClO < HOClO_2 < HOClO_3$

22.4.3 Chlorofluorocarbons (CFC)

Chlorofluorocarbons are the compounds of carbon where chlorine and fluorine are substituted for hydrogen in saturated hydrocarbons e.g. CCl_2F_2 , $CFCl_3$, $C_2F_4Cl_2$ etc. These compounds have very high capacity to retain heat. It is believed that the capacity to retain heat is about 10,000 times more than that of carbon-dioxide. Thus these molecules are capable of cooling other systems by taking away their heat.

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

22.4.4 Interhalogen Compounds

The halogens form a series of mixed binary compounds called the interhalogens. These compounds are of the type XX', XX_3' , XX_5' , and XX_7' . The compounds of the type XX' are known for all combinations. Compounds of XX_3' , and XX_5' types are known for some,

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and of XX_7' type only IF_7 is known.

Preparation

The interhalogen compounds can be prepared by direct reaction between the halogens. They can also be prepared by the action of a halogen on a lower interhalogen.

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Cl_2 + F_2 (equal volumes) \xrightarrow{473K} 2CIF
Cl_2 + 3F_2 \text{ (excess } F_2) \xrightarrow{573K} 2CIF_3
l_2 + 5F_2 \xrightarrow{293K} 2IF_5
l_2 + 7F_2 \xrightarrow{523-573K} 2IF_7
     Intext Questions 22.4
 Name the most electronegative halogen.
1.
   Name the halogen that can react with an inert gas.
2.
       .....
  Write a chemical reaction used for the laboratory preparation of chlorine.
3.
  .....
  Arrange the hydroacids of halogens in the decreasing order of their strength.
4.
  .....
  What group of carbon compounds is supposed to cause ozone depletion.
5.
  .....
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22.5 Compounds of Noble Gases

The group 18 of the periodic table consists of six elements – helium, neon, argon, krypton, xenon and radon. These elements are termed as **'noble gases'**. The name noble gases implies that they tend to be unreactive and are reluctant to react just like noble metals. Except helium which has 2 electrons and forms a complete shell 1s², the other elements of the group have a closed octet of electrons in their outer shell ns² np⁶. This electronic configuration is very stable and the ionization energies of the atoms of these elements are very high. Therefore, the atoms of noble gases have a little tendency to gain or lose electrons. Hence these elements exhibit lack of chemical reactivity.

The first compound of noble gases was made by Neil Bartlett in 1962 by the reaction of xenon with PtF_6 . Since then several other xenon compounds, mainly with the most electronegative elements (fluorine and oxygen), have been prepared. He, Ne and Ar do not form any compounds whereas Kr does form KrF₂. Radon is a radioactive element and all its isotopes have very short half lives.

Xenon Compounds

Xenon reacts with fluorine to form binary fluorides, XeF_2 , XeF_4 and XeF_6 . The product formed depends on the temperature and xenon-fluorine ratio. Thus

 $Xe + F_2 \xrightarrow{873 \text{ K}, 1 \text{ bar}} XeF_2(s)$

(2:1 ratio)

 $Xe + 2F_2 \xrightarrow{873 \text{ K}, 7 \text{ bar}} XeF_4(s)$

(1:5 ratio)

 $Xe + 3F_2 \xrightarrow{573 \text{ K}, 60 \text{ bar}} XeF_6$ (s)

(1:20 ratio)

 XeF_2 , XeF_4 and XeF_6 are all white solids. They readily sublime at 298 K. They differ in their reactions with water

XeF₂ dissolves in water and undergoes slow hydrolysis in water.

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

 XeF_4 and XeF_6 react with water violently to give xenon trioxide and hydrogen fluoride.

 $6 \operatorname{XeF}_4 + 12H_2O \longrightarrow 4 \operatorname{Xe} + 2\operatorname{XeO}_3 + 24 \operatorname{HF} + 3O_2$

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

 XeF_{6} on partial hydrolysis gives, xenon oxofluorides.

 $XeF_6 + H_2O \longrightarrow XeOF_4 + 2HF$

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

The xenon fluorides react with strong Lewis acids to form complexes.

$$XeF_2 + PF_5 \longrightarrow [XeF]^+ [PF_6]^-$$

 $XeF_4 + Sb F_5 \longrightarrow [XeF_3]^+ [SbF_6]^-$

 XeF_{6} may also act as a fluoride accepter from fluoride ion donors to form fluoroxenate anions.

 $XeF_6 + MF \longrightarrow M^+[XeF_7]^- (M = Na, K, Rb, Cs)$

 XeO_3 can be prepared by hydrolysis of XeF_6

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

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XeO₄ can be prepared by the reaction of barium peroxenate with conc. sulphuric acid

$$Ba_2XeO_6 + 2H_2SO_4 \longrightarrow XeO_4 + 2BaSO_4 + 2H_2O_4$$

Structure of Xenon compounds

The structures and shapes of the common xenon fluorides and oxides are shown below. The shapes of these molecules can be explained in terms of VSEPR theory which you have already learnt in chemical bonding.



Fig. 22.3 : The structures of XeF_2 , XeF_4 , XeF_6 , XeO_3 and $XeOF_4$

🕉 What You Have Learnt

- While sulphur exists as S_8 molecules oxygen exists as O_2 molecules. Both these elements form divalent anions however sulphur also shows +4 and +6 oxidation state. Oxygen and sulphur are non-metals of group number 16.
- The binary compounds of oxygen with other elements are known as oxides. The oxides can be classified as : acidic oxides, basic oxides and amphoteric oxides.
- Ozone, an allotrope of oxygen is prepared by Siemen's ozonizer.
- Sulphuric acid displays strong acid character and possesses oxidizing and dehydrating properties.
- Chlorine forms a number of oxoacids : HOCl, HClO₂, HClO₃ and HClO₄.

- The binary compounds of halogens with one another are called inter halogen compounds.
- Halogens are placed in group number 17 of the periodic table. All members of the group are very reactive. They show variable oxidation states. Halogens react with other halogen forming interhalogens. Halogen (Fluorine) can even react with noble gases. Halogens react with hydrogen forming hydracids.
- Fluorochlorocarbons are called freons which decompose ozone and are therefore environmentally hazardous.
- Helium, neon, argon, krypton, xenon and radon are the members of Group number 18 and are collectively called noble gases.
- Xenon is known to react with fluorine to form XeF_2 , XeF_4 and XeF_6 .

Terminal Exercises

- 1. Which one of the following oxides can react with an acid as well as with an alkali : SO₂, CaO, ZnO, MgO?
- 2. Write two oxides which do not react with either acids or alkalies. Which type of oxides are they?
- 3. Is ozone an allotrope of oxygen? Which is more soluble in water oxygen or ozone?
- 4. What is the state of hybridization of the central oxygen atom in O_3 molecule?
- 5. Why does ozone tail mercury?
- 6. Which property of ozone makes it useful for bleaching?
- 7. Write the conditions which are required to convert SO₂ to SO₃ in the manufacture of sulphuric acid by contact process.
- 8. What is oleum?
- 9. Why is sulphuric acid known as king of chemicals?
- 10. Fluorine never acts as a central atom in any interhalogen compounds. Why?
- 11. Draw the structure of BrF_4^- .
- 12. Arrange the hydrogen halides in order of their acid strength in aqueous solution.
- 13. Why is F_2O not known as fluorine oxide? Instead it is known as oxygen fluoride, OF_2 .
- 14. Which is the strongest acid among the oxoacids of chlorine and why?
- 15. What happens when XeF_4 reacts with SbF_5 ? Write the complete equation for the reaction.

Answers to Intext Questions

22.1

1. Basic oxide : CaO; acidic oxide : SO_2 ; amphoteric oxide : ZnO.

MODULE-6

Chemistry of Elements



Notes

MODULE-6 Ch

Chemistry

Chemistry of Elements



Acidic oxide : SiO₂, SO₂, CrO₃
 Basic oxide : K₂O, FeO
 Amphoteric oxide : Al₂O₃, ZnO

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3. $ZnO + H_2SO_4 \longrightarrow ZnSO_4 + H_2O$ $ZnO + 2NaOH \longrightarrow Na_2Zn O_2 + H_2O$ 4. An oxide of group 1, K₂O and of Gr 2 BaO $K_2O + 2HCl \longrightarrow 2KCl + H_2O$ $BaO + H_2SO_4 \longrightarrow BaSO_4 + H_2O$ 22.2 When ethene combines with O_3 , an ozonide is formed, thus $CH_2 = CH_2 + O_3 \longrightarrow O$ On hydrolysis it gives HCHO, $\begin{array}{c} CH_2 - O - CH_2 &+ H_2O \longrightarrow 2HCHO + H_2O_2 \\ O & \longrightarrow O \end{array}$ 2. (i) $2\text{FeSO}_4 + \text{O}_3 + \text{H}_2\text{SO}_4 \longrightarrow \text{Fe}_2(\text{SO}_4)_3 + \text{H}_2\text{O} + \text{O}_2$ (ii) $3SnCl_2 + O_3 + 6HCl \longrightarrow 3SnCl_4 + 3H_2O$ 3. Ozone is 10 times more soluble than O_2 . 4. $O_{117^{\circ}O}^{0}O_{128pm} O_{resonance hybrids}^{0}O_{resonance hy$ 5. Mercury loses its convex meniscus and leaves a "tail" or a trail of minute droplets on a glass surface when exposed to ozone. This is due to the formation of mercurous oxide. The tailing effect can be removed by washing the mercury with a dilute acid. 22.3

1 (i) Oxidizing property of conc. H_2SO_4

 $\mathrm{Cu} + 2\mathrm{H_2SO_4} \longrightarrow \mathrm{CuSO_4} + \mathrm{SO_2} + 2\mathrm{H_2O}$

(ii) Dehydrating property : It removes water from sugar

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

2. A corrosive mist of sulphuric acid is formed.

3.
$$2SO_2 + O_2 \xrightarrow{V_2O_5} 2SO_3$$

22.4

- 1. Fluorine
- 2. Fluorine
- 3. 2 NaCl + $3H_2SO_4$ + MnO₂ \longrightarrow MnSO₄ + 2NaHSO₄ + $2H_2O$ + Cl₂
- 4. Hl > HBr > HCl > HF
- 5. Chlorofluorocarbons (or freons)



MODULE-6

