



Notes



313en20

20

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:

- explain general characteristics of group 16, 17 and 18 elements;
- classify oxides into acidic, basic and amphoteric types;
- recall the preparation, properties and uses of ozone;
- explain the allotropic forms of sulphur;
- describe the manufacture of sulphuric acid;
- proportion properties and uses of SO_2 ;
- structure oxoacids of sulphur;
- 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;
- explain occurrence 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 .

20.1 SOME CHARACTERISTIC PROPERTIES OF THE ELEMENTS OF GROUP 16

The Group 16 elements show the usual gradation from non metallic to metallic properties with increasing atomic number that occurs in any periodic group. Oxygen and sulphur are non-metals, selenium and tellurium are semiconductors and polonium is metallic.

These elements can enter into chemical combination and complete their octets by gaining two electrons to form the 2 di-valent ions, e.g. O^{2-} , S^{2-} , except for polonium which is too metallic, or by forming two covalent bonds, e.g. the hydrides H_2O , H_2S , H_2Se , H_2Te and H_2Po .

The two heavier members of this group can form the 4-valent cation X^{4+} e.g. there is evidence of the presence of Te^{4+} ions in the dioxide TeO_2 and of Po^{4+} ions in the dioxide, PoO_2 , and sulphate, $Po(SO_4)_2$.

Because sulphur, selenium, tellurium and polonium have vacant *d* orbitals that can be utilised without too great an energy change, they are able to form covalent compounds in which the octet of electrons is expanded; for instance, the valencies of sulphur in H_2S , SCl_4 and SF_6 are two, four and six, respectively. Oxygen, in common with other first row members of the Periodic Table, cannot expand its octet.

Oxygen exists in the form of discrete molecules, a double bond uniting two oxygen atoms together, $O = O$. The atoms of the other Group elements do not form multiple bond to themselves and sulphur, in particular, shows a strong tendency to catenate, puckered S_8 rings being present in rhombic and monoclinic sulphur. There are two forms of selenium corresponding in structure to rhombic and monoclinic sulphur in which Se_8 rings, are present. These forms, however, are readily converted into a 'metallic' form of the element called grey selenium. As far as is known, there is only one form of tellurium which has the same structure as grey selenium. Polonium is truly metallic.

Table 20.1: Properties of Group 16 elements

	Atomic Number.	Electronic Configuration	Atomic Radius/nm	Ionic Radius/nm	M.P. /°C	B.P. /°C
O	8	2.6 $1s^2 2s^2 2p^4$	0.074	0.140	-218	-183
S	16	2.8.6 $\dots 2s^2 2p^6 3s^2 3p^4$	0.104	0.184	119*	445
Se	34	2.8.18.6 $\dots 3s^2 3p^6 3d^{10} 4s^2 4p^4$	0.117	0.198	217**	685



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MODULE - 6

Chemistry of Elements



Notes

p-block Elements and Their Compounds - II

Te	52	2.8.18.18.6 ... $4s^2 4p^6 4d^{10} 5s^2 5p^4$	0.137	0.221	450	990
Po	84	2.8.18.32.18.6 ... $5s^2 5p^6 5d^{10} 6s^2 6p^4$	0.140		254	960

* For monoclinic sulphur

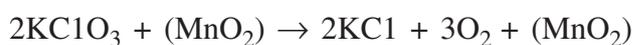
** For grey selenium

Occurrence

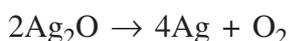
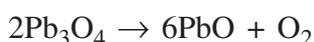
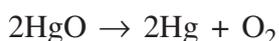
Oxygen occurs in the atmosphere to the extent of about 21 per cent by volume (23 per cent by weight). This percentage remains constant by the operation of the highly complex process termed photosynthesis. The element is present in the earth's crust and in water to the extent of about 50 per cent and 89 per cent by weight, respectively. It is an essential ingredient in all living matter and is of prime importance in respiration and combustion processes. Although only slightly soluble in water, enough oxygen dissolves to support marine life.

Preparation of dioxygen

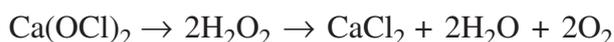
1. By heating chlorates, nitrates and permanganates :



2. By heating metallic oxides :



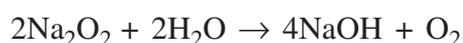
3. By the action of bleaching powder on hydrogen peroxide solution.



4. By the action of hot and concentrated sulphuric acid on potassium dichromate or potassium permanganate.



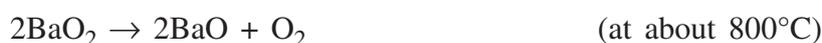
5. By the action of sodium peroxide on water.



Manufacture of oxygen :

(1) **By the electrolysis of water :** Where ever electricity is cheap, oxygen can be conveniently manufactured by the electrolysis of water. The electrolysis is carried out in iron tanks containing a solution of caustic soda or acidified water. The electrodes used are of iron or nickel and a current of 1000 amperes is used. Oxygen is evolved at the anode and hydrogen at the cathode. A porous diaphragm is used to prevent the mixing of hydrogen and oxygen.

2. **From air :** When barium oxide is heated in air to about 500°C it combines with oxygen to form barium peroxide, BaO₂. On raising the temperature to about 800°C, the peroxide decomposes to give barium oxide and oxygen.



It can be prepared from liquified air. There is a difference of 12.5°C in the boiling points of oxygen and nitrogen ; oxygen boils at -182.5°C while nitrogen at -195°C. This difference is sufficient to enable a separation of the two by fractional distillation.

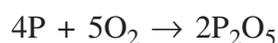
PROPERTIES**Physical**

Oxygen is colourless, tasteless and odourless gas and slightly heavier than air. Liquid oxygen is pale blue with boiling point -182.5°C and specific gravity 1.2386 at -210°C. The liquid solidifies on cooling at -218.4°C to a light blue solid. It is somewhat soluble in water (about 3%), a fact responsible for aquatic life. Liquid oxygen is paramagnetic and is strongly attracted by magnet.

Chemical

Oxygen is essentially required for the burning or combustion of substances in air. Combustion is much more brilliant in pure oxygen. Molecular oxygen combines directly with most of the elements, exceptions being the inert gases, the halogens, gold and platinum. It is a fairly good oxidising agent in aqueous solution and directly oxidises Cr²⁺, Fe²⁺, SO₃²⁻, V²⁺, and Ti³⁺ ions. The gas oxidises some substances at ordinary temperature, some at higher temperatures, and some in presence of suitable catalysts.

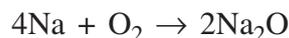
(i) *At ordinary temperatures :* Phosphorus is slowly oxidised in oxygen to form its pentoxide at room temperature. The oxidation of alkali and alkaline earth metals and the rusting of iron take place at ordinary temperatures. Nitric oxide quickly combines with oxygen to give brown fumes of dioxide, NO₂



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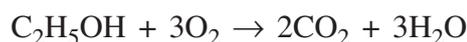
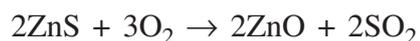
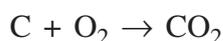
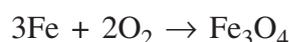


Notes



One of the most important reactions of molecular oxygen is the one that takes place between the inspired oxygen and the protein haemoglobin at the body temperature.

(ii) *At higher temperatures* : At higher temperatures it combines with almost all the elements to form compounds with the evolution of much energy. The binary compounds so obtained are known as oxides.



Uses : Apart from it being an absolute necessity for terrestrial life, oxygen is used for many industrial purposes.

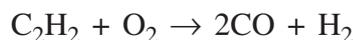
(i) *For the production of high temperature flames* :

Oxy-hydrogen flame = 2400°—2800°C

Oxy-coal gas flame = 2200°—2400°C

Oxy-acetylene flame = 3100°—3300°C

Oxy-acetylene flame produces hydrogen which prevents the oxidation of metals during welding or cutting.



(ii) *For medical purposes* : When even a patient is unable to breath sufficient air, oxygen is given for artificial respiration.

(iii) *In iron and steel industry* : Addition of oxygen to the air blast in blast furnace raises the temperature required for the manufacture of iron and steel.

(iv) *In rocket fuels* : Liquid oxygen is an important constituent of the fuels used in rockets.

(v) It is also used for bleaching purposes.

(vi) Oxygen is used as an oxidizing agent in laboratories and in many industries.

20.2 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.



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20.2.1 Classification of Oxides

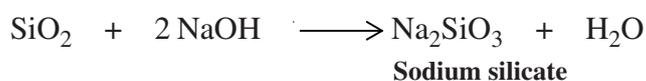
The binary compounds of oxygen with other elements (metals or non-metals) are called oxides. An understanding of the nature of an oxide provides a clue to the nature of the element which forms the oxide. Depending upon the acid-base behaviour of the oxides, they can be classified into the following categories.

- (1) Acidic oxides
- (2) Basic oxides
- (3) Amphoteric oxides
- (4) Neutral oxides

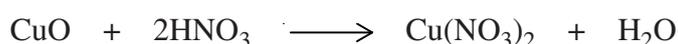
(1) Acidic Oxides : Acidic oxides are generally formed by non-metallic elements and some metals in higher oxidation states. Examples of some acidic oxides are CO_2 , SO_2 , N_2O_5 , P_4O_{10} , Cl_2O_7 , Mn_2O_7 , etc. These oxides combine with water to form acids whereas with alkalis they form salt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



However, certain acidic oxides do not form acids on reacting with water. But they react with alkalis to form salt and water, e.g., SiO_2



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



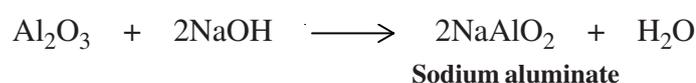
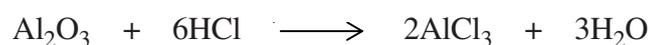
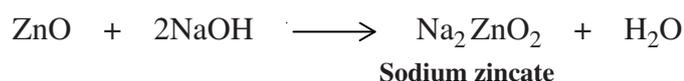
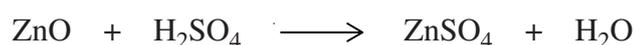
The oxides of the metals of Groups 1 and 2 react with water to form hydroxides known as **alkalis**.





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(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.



(4) Neutral oxides : These oxides are neither acidic nor basic. Examples are carbon monoxide, (CO), nitric oxide (NO), nitrous oxide (N₂O), etc.



INTEXT QUESTIONS 20.1

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.
4. Name the compound formed when the oxide of an element of Group 1 or 2 reacts with acid?
5. Oxygen is a gas but Sulphur is solid why?

20.3 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.

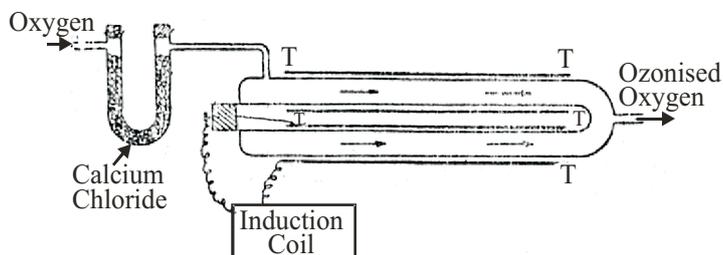
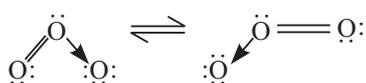


Fig. 20.1 : Siemen's Ozonizer

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.

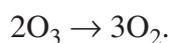
All rubber and cork fittings are avoided because of the corrosive action of ozone on these materials.

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.
- 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.



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



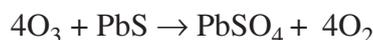
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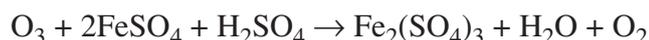
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In most of the reactions, oxygen gas is liberated as the reduction product from ozone.

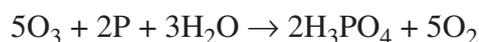
- (i) It oxidizes black lead sulphide to white lead sulphate



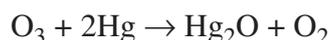
- (ii) Ozone oxidizes acidified ferrous sulphate to ferric sulphate



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



- (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.

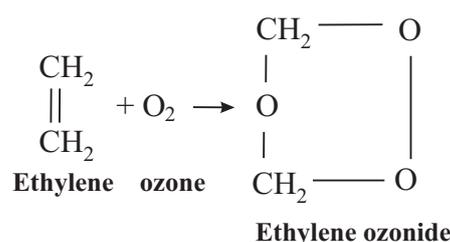


The 'tailing' effect can be removed by washing with dilute acid.

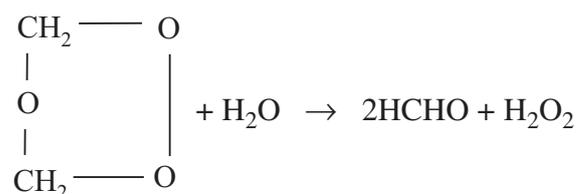
- (v) Ozone oxidizes stannous chloride to stannic chloride. Note that no oxygen is produced in this reaction.



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.



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

Uses of Ozone

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 20.2**

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
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?

20.4 ALLOTROPIC FORMS OF SULPHUR**Rhombic sulphur**

This is the form of sulphur normally encountered and consists of S_8 structural units packed together to give crystals whose shape is shown in Fig. Fairly large crystals can be obtained by allowing a solution of powdered sulphur in carbon disulphide to evaporate slowly; they are yellow, transparent and have a density of 2.06 g cm^{-3} .



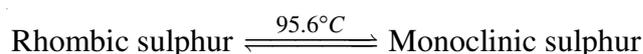
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Monoclinic sulphur

This form of sulphur is formed when molten sulphur is allowed to crystallise above 95.6°C. Like rhombic sulphur it consists of S₈ structural units, but these are arranged differently in the crystal lattice. The temperature of 95.6°C is the transition temperature for sulphur; below temperature, 95.6°C rhombic sulphur is the more stable allotrope and above it, the monoclinic sulphur is the more stable of the two forms.



Crystals of monoclinic sulphur are amber-yellow in colour and have a density of 1.96 g cm⁻³.

Amorphous sulphur

A number of forms of sulphur which possess no regular crystalline form can be obtained when sulphur is liberated in chemical reactions, e.g. by the action of dilute hydrochloric acid on a solution of sodium thio-sulphate:

**Plastic sulphur**

This is obtained, by pouring nearly boiling sulphur into cold water. It consists of a completely random arrangement of chains of sulphur atoms which, when stretched, align themselves parallel to each other. On standing, it slowly changes over into rhombic sulphur, as the chains of sulphur atoms break and reform the S₈ cyclic units.

The action of heat on sulphur

Both rhombic and monoclinic sulphur melt to a yellow liquid. Owing to the conversion of rhombic to monoclinic sulphur, and also to possible variations in the percentage of allotropes of liquid sulphur formed, the melting points are not sharp: rhombic sulphur melts at approximately 113°C and monoclinic sulphur at approximately 119°C. As the temperature rises the colour of the liquid darkens until it is nearly black, and it becomes viscous. At about 200°C the viscosity begins to fall and at its boiling point of 445°C the liquid is again mobile.

There is still some doubt concerning a complete explanation of these observations, but a recent theory runs as follows: as the sulphur melts the S₈ rings begin to open and it is possible that other ring systems containing possibly six and four sulphur atoms form. It is known, however, that sulphur chains begin to form and reach their maximum chain length at 200°C, corresponding to the maximum viscosity of liquid sulphur. The decrease in viscosity of liquid sulphur that occurs above 200°C is explained as being due to the breakdown of these long chains and the re-formation of S₈ rings. Sulphur vapour contains S₈ rings, together

with smaller fragments such as S₈, S₄ and S₂. At very high temperatures atomic sulphur is formed.

Sulphur Dioxide, SO₂

Priestley (1774) obtained this gas by heating mercury with concentrated sulphuric acid and called it *vitriolic acid air*. Lavoisier in 1777 determined its composition.

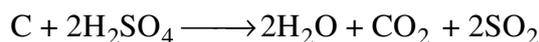
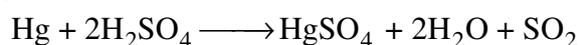
It is found in volcanic gases and in traces in the air of towns; being derived from the burning of iron pyrites present as impurity in coal.

Preparation : *By the reduction of sulphuric acid* ' It is prepared in the laboratory by reducing hot concentrated sulphuric acid with copper turnings.

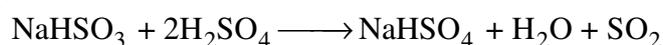


The gas is dried by concentrated sulphuric acid, calcium chloride or phosphorus pentoxide and is collected by upward displacement of air or over mercury.

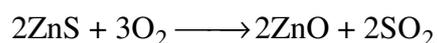
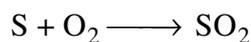
The reduction of concentrated sulphuric acid may also be brought about by heating with mercury, silver, sulphur or charcoal.



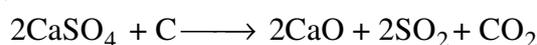
(ii) *By the action of alkali on sulphites or bisulphites :*



(iii) *By burning sulphur or sulphide ores :*



(iv) Now-a-days, it is commercially prepared by heating *anhydrite* (CaSO₄) with clay and coke at 1200°C.



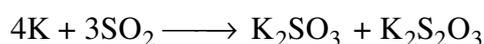
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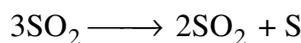
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Properties : It is a colourless gas with an odour well known as that of burning sulphur. It is $2\frac{1}{4}$ times as heavy as air. It is easily liquified by compression (2.5 atm at 15°C) or by cooling in a freezing mixture. Its critical temperature is 157.15°C and critical pressure 77.65 atm. The liquid is colourless, boils at -10°C and freezes at -75.5°C . Liquid sulphur dioxide is a good solvent for iodine, sulphur, phosphorus etc.

(i) *Incombustible and non-supporter of combustion :* It is incombustible and does not support combustion in the ordinary sense, but heated potassium, magnesium, tin and iron burn in the gas.

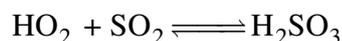


(ii) *Decomposition :* When heated to 1200°C it decomposes to an appreciable extent giving sulphur trioxide and sulphur.

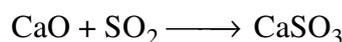


It is also decomposed in a strong beam of light.

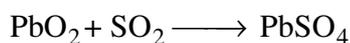
(iii) *Acidic nature :* It is highly soluble in water forming unstable sulphurous acid.



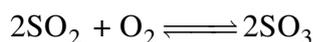
Being an acidic oxide, it combines with basic oxides forming sulphites, e.g.,



(iv) It combines with certain metallic dioxides yielding metallic sulphates, e.g.,

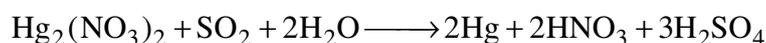
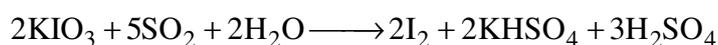
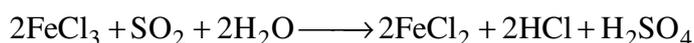
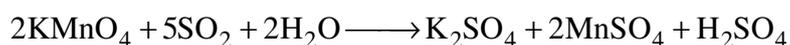
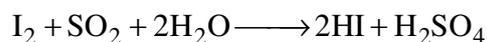


(v) It combines with oxygen and with chlorine

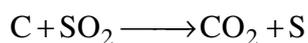


(vi) *Reducing properties :* In presence of moisture, it acts as a fairly strong reducing agent. For example





(vii) *Oxidising properties* : It also acts as an oxidising agent. Such as



(viii) *Bleaching properties* : In presence of moisture it acts as a mild bleaching agent;



the nascent hydrogen bleaches the colour of the substance. Thus sulphur dioxide bleaches by *reduction*

Uses:

It is used

- (i) in the manufacture of sulphuric acid.
- (ii) in the refining of sugar and kerosene oil.
- (iii) in fumigation and in preserving fruits since it has antiseptic properties.
- (iv) As a refrigerant in the liquid state.
- (v) For bleaching delicate articles such as wool, silk and straw.
- (vi) In the preparation of sodium and calcium bisulphites which are used in paper industry.
- (viii) As an *antichlor* in removing excess chlorine from bleached materials.



Notes

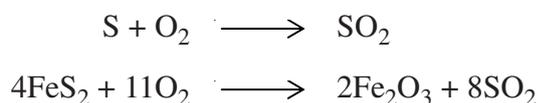
20.5 SULPHURIC ACID

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.

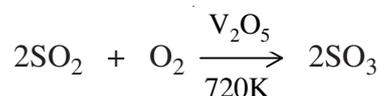
Manufacture : The two main processes used for the manufacture of sulphuric acid are (1) Lead Chamber process and (2) the Contact process. Nowadays sulphuric acid is mostly manufactured by Contact process.

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.

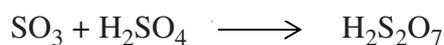


- (ii) Sulphur dioxide produced is then freed from dust and other impurities such as arsenic compounds.
- (iii) The purified sulphur dioxide is then oxidized by atmospheric oxygen to sulphur trioxide in the presence of a catalyst, vanadium (V) oxide, V_2O_5 heated to 720K.



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

- (iv) The sulphur trioxide gas is then absorbed in conc. H_2SO_4 to form *oleum* ($\text{H}_2\text{S}_2\text{O}_7$). If SO_3 is directly dissolved in water, a highly corrosive mist of sulphuric acid is formed.



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



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



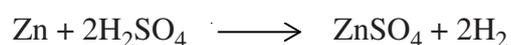
Notes

liberation of a 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.

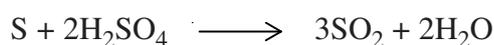
Chemical properties : The most important properties of sulphuric acid are its oxidizing and dehydrating properties.

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

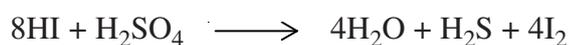
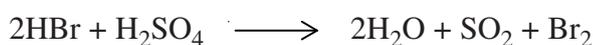
Oxidation of metals.



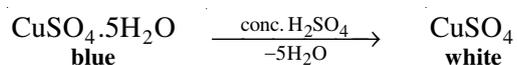
Oxidation of non-metals



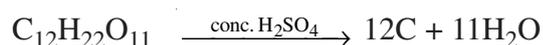
Oxidation of compounds



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.



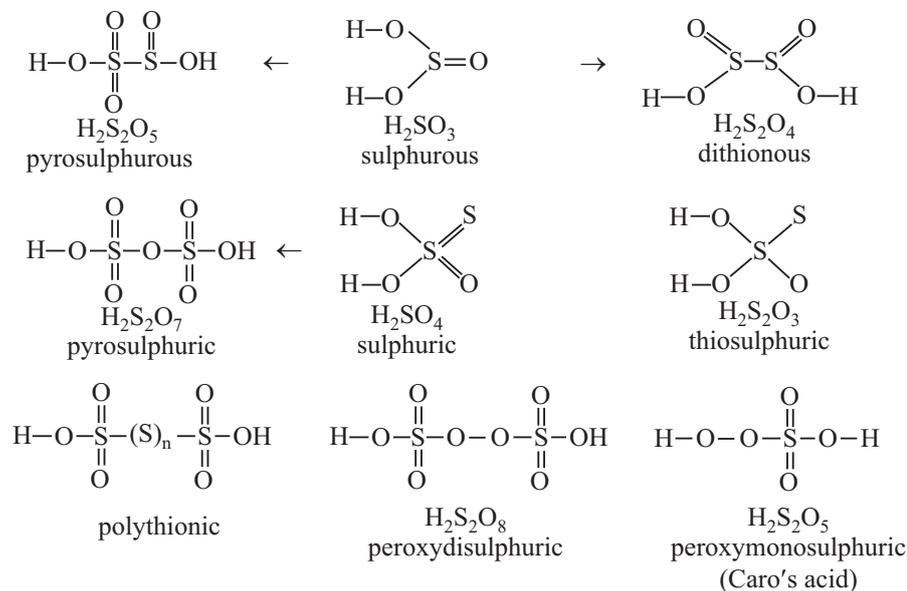
Uses of Sulphuric Acid

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.



Notes

Structures of Oxyacids of Sulphur



Notes

Fig. 20.2: Some oxyacids of sulphur.



INTEXT QUESTIONS 20.3

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

20.6 SOME GENERAL CHARACTERISTIC PROPERTIES OF ELEMENTS OF GROUP 17

All members of Group 17 are non-metallic, although there is the usual increase in 'metallic' character with increasing atomic number, e.g. dipyrindine iodine nitrate can be written as $[\text{I}(\text{pyridine})_2]^+\text{NO}_3^-$, containing the 1^+ ion as part of a complex. Fluorine and chlorine are gases, bromine is a volatile liquid, and iodine is a dark shiny coloured solid. Astatine is radioactive and very short-lived; what little chemistry that has been carried out with this element has employed tracer techniques.

These elements can enter into chemical combination and complete their octets by gaining one electron to form the 1-valent ion, e.g. F^- , Cl^- , etc., and by forming one covalent bond, e.g. the elements themselves F_2 , Cl_2 , Br_2 , I_2 and their hydrides HF, HCl, HBr and HI.

Because chlorine, bromine and iodine have easily accessible *d* orbitals available, they are able to form covalent compounds in which the octet of electrons is expanded; for instance, iodine shows valencies of 1, 3, 5 and 7 respectively in the compounds ICl, ICl_3 , IF_5 and IF_7 . Like nitrogen and oxygen (the first members of Group 15 and 16, respectively), fluorine cannot expand its octet and is thus restricted to a covalency of 1.

The molecules of the halogens are diatomic with only weak van der Waals' forces operating between the individual molecules; however, in the case of iodine these forces are sufficiently strong to bind the iodine molecules into a three dimensional lattice (fig.). This structure is easily broken down on heating, and in fact, iodine sublimes at one atmosphere pressure if warmed gently.

The Structure of iodine

There is sufficient difference between fluorine and chlorine in chemical behavior to warrant a separate treatment of the former element. Chlorine, bromine and iodine are treated as a group.

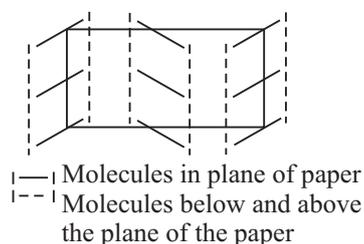


Table 20.2: Physical properties of Group 17 elements

	Atomic Number	Electronic Configuration	Atomic Radius/nm	Ionic Radius/nm M^{3+}	M.P. /°C	B.P. /°C
F	9	2.7 ... $1s^2 2s^2 2p^5$	0.072	0.136	-220	-188
Cl	17	2.8.7 ... $2s^2 2p^6 3s^2 3p^5$	0.099	0.181	-101	-34.7
Br	35	2.8.18.7 ... $3s^2 3p^6 3d^{10} 4s^2 4p^5$	0.114	0.195	-7.2	58.8
I	53	2.8.18.18.7 ... $4s^2 4p^6 4d^{10} 5s^2 5p^5$	0.133	0.216	114	184
At	85	2.8.18.32.18.5 ... $5s^2 5p^6 5d^{10} 6s^2 6p^5$				



Notes



Notes

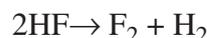
Occurrence

Fluorine and chlorine are fairly abundant, bromine and iodine less so. Fluorine is present mainly in the insoluble fluorides of calcium: calcium fluoride; cryolite, Na_3AlF_6 ; and fluoroapatite, $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaF}_2$. Sea-water contains the chlorides, bromides, and iodides, of sodium, potassium, magnesium, and calcium. The deposits of dried-up seas contain these compounds, mainly the chlorides, for example sodium chloride and carnallite, $\text{KCl} \cdot \text{MgCl}_2$. Certain forms of marine life concentrate iodine in their systems.

20.7 FLUORINE AND CHLORINE

Fluorine and chlorine are the first two members of Group 17. 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 (KHF_2) in anhydrous hydrogen fluoride. Hydrogen fluoride undergoes electrolytic dissociation.

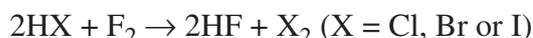


The fluorine obtained is contaminated with hydrogen fluoride which may be removed by passing the gas over solid NaF .

Fluorine is a pale yellow gas which fumes in air.

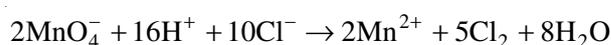
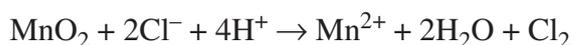


Fluorine is highly reactive. It combines with various metals and non-metals to form fluorides. With hydrogen halides it acts as an oxidizing agent, e.g.



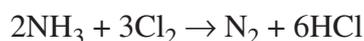
Fluorine is widely used in the preparation of fluorinated hydrocarbons which in turn find various uses in industry.

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



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



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



Notes

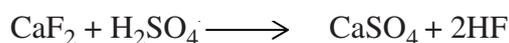
20.7.1 Hydrogen Halides and Hydrohalic Acids

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 < HI

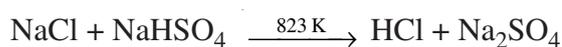
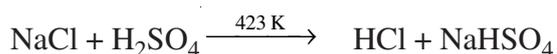
The aqueous solutions of hydrogen halides are, in general, known as hydrohalic acids or simply halogen acids (hydrofluoric, hydrochloric hydrobromic, and hydroiodic acids)

Preparation of Hydrogen Halides

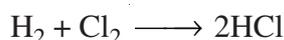
Industrially HF is made by heating CaF_2 with strong H_2SO_4 .



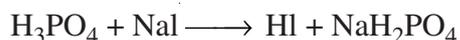
Hydrogen chloride is made by heating a mixture of NaCl and conc. H_2SO_4 at 423 K.



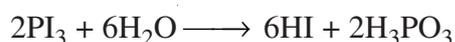
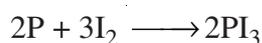
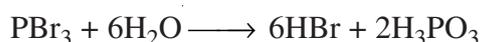
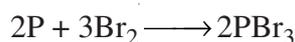
High purity HCl is made by the direct combination of the elements (H_2 and Cl_2)



Phosphoric acid is used to make HI



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





Notes

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. 20.2).

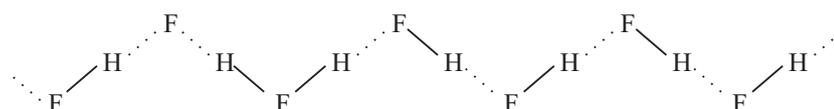


Fig. 20.2 : Hydrogen bonded chain in HF

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



The bond dissociation energy of the hydrogen halides follow the order $\text{HF} > \text{HCl} > \text{HBr} > \text{HI}$.

The stability of hydrogen halides to thermal decomposition therefore decreases in the order $\text{HF} > \text{HCl} > \text{HBr} > \text{HI}$. The acid strength of the acids increases in the order $\text{HF} < \text{HCl} < \text{HBr} < \text{HI}$. 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.

20.7.2 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.



Notes

Oxides of chlorine The main oxides are listed below :

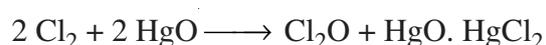
Chlorine monoxide, Cl_2O

Chlorine dioxide, ClO_2

Chlorine hexoxide, Cl_2O_6

Chlorine heptoxide, Cl_2O_7

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



It is a pale yellow gas which decomposes violently on heating and dissolves in water forming hypochlorous acid. $\text{Cl}_2\text{O} + \text{H}_2\text{O} \longrightarrow 2\text{HOCl}$

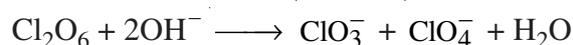
It is a powerful oxidizing agent.

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

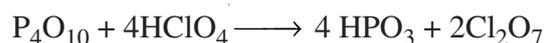


It is an orange gas and explosive in nature.

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 alkalis producing chlorate and perchlorate

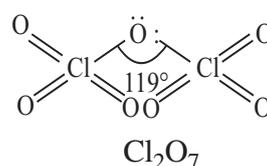
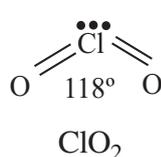
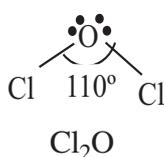


Chlorine heptoxide, Cl_2O_7 , is prepared by the action of phosphorus pentoxide on anhydrous perchloric acid at 263 K.



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

The structures of chlorine oxides are as follows :



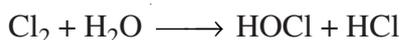


Notes

Oxoacids of chlorine

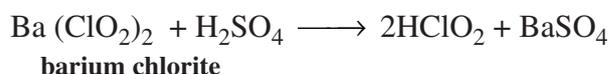
Chlorine forms four oxoacids, HOCl, HOClO, HOClO₂ and HOClO₃

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

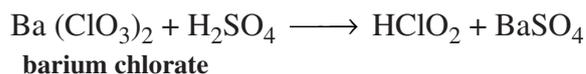


Its salt NaOCl is used as a bleaching agent.

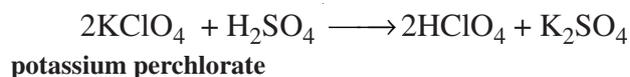
Chlorous acid, HOClO is also known in solution, certain chlorite salts of alkali and alkaline earth metals are known in solid state, e.g., NaClO₂·3H₂O. The acid is prepared by the action of barium chlorite with sulphuric acid.



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



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



It is a colourless oily liquid and combines vigorously with water forming hydronium perchlorate (H₃O⁺ 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 20.3 : Oxoacids of chlorine

Name	Hypochlorous acid (a)	Chlorous acid (b)	Chloric acid (c)	Perchloric acid (d)
Formula of oxoacid	HOCl	HOClO	HOClO ₂	HOClO ₃
Oxidation state of chlorine	+1	+3	+5	+7
Structure				

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 than 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 HOClO_3 require the least energy to break the O–H bond and form H^+ . Thus, HOCl is a very weak acid whereas HOClO_3 is the strongest acid, thus the acid strength increases in the order.



20.7.3 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 , $\text{C}_2\text{F}_4\text{Cl}_2$ 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.

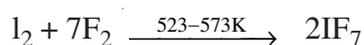
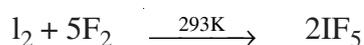
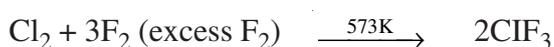
Chlorofluorocarbons are also termed as **freons**. About 5 thousand metric tonnes of CFC's are still being produced in our country annually. In addition to their usage as aerosols, solvents, foam blowing agents and refrigerants, they are also known to cause environmental hazard. CFCs react with protective 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.

20.7.4 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, 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.



Notes



INTEXT QUESTIONS 20.4

1. Name the most electronegative halogen.
2. Name the halogen that can react with an inert gas.
3. Write a chemical reaction used for the laboratory preparation of chlorine.
4. Arrange the hydroacids of halogens in the decreasing order of their strength.
5. What group of carbon compounds is supposed to cause ozone depletion.



Notes

20.8 THE NOBLE GASES

The gaseous elements helium, neon, argon, krypton, xenon and radon constitute the 18 group of the periodic table. Because of their low abundance on the earth, they have been called *rare gases*, and due to their chemical inertness, they have been called inert or noble gases. With the discovery that some of them can form compounds under suitable conditions, we no longer refer to them as inert gases. All of them, except helium, have the closed shell, np^6 , configurations. Helium has the $1s^2$ configuration. The electronic configuration accounts for their high degree of chemical inertness in ordinary chemical reactions.

Occurrence

All the noble gases, except radon, are present in atmosphere. The relative percentages of the noble gases in dry air are given in the following table.

Table 20.4: Relative Abundance of 18 Group Elements in Dry Air

Element	Percentage
Helium (He)	5.2×10^{-4}
Neon (Ne)	1.8×10^{-3}
Argon (Ar)	9.3×10^{-1}
Krypton (Kr)	1.1×10^{-4}
Xenon (Xe)	8.7×10^{-6}
Radon (Rn)	—

In addition helium is present up to 10 per cent in natural gas. It also results from the decay of certain radioactive elements and is found in some uranium minerals. Radon is produced in the radioactive decay of radium.

Properties

The outer electronic configuration and the general trends in properties of the noble gases are summarised in Table

Table 20.5: Relative Abundance of 18 Group Elements in Dry Air

***	He	Ne	Ar	Kr	Xe	Rn*
Atomic number	2	10	18	36	54	86
Atomic mass	4.00	20.18	39.95	83.80	131.30	222.00
Electronic configuration	$1s^2$	[He] $2s^2 2p^6$	[Ne] $3s^3 3p^6$	[Ar] $3d^{10} 4s^2 4p^6$	[Kr] $4d^{10} 5s^2 5p^6$	[Xe] $4f^{14} 5d^{10} 6s^2 6p^6$
Atomic radii	120	160	190	200	220	-
Ionic radii/kJmol ⁻¹	2372	2080	1520	1351	1170	1037
Election gain enthalpy/kJmol ⁻¹	48	116	96	96	77	68
Den (at STP)/gcm ⁻³	1.8×10^{-4}	9.0×10^{-4}	1.8×10^{-3}	3.7×10^{-3}	5.9×10^{-3}	9.7×10^{-3}
M.P.	-	24.6	83.8	115.9	161.3	202
B.P.	4.2	27.1	87.2	119.7	165.0	211
Fraction in Air (% volume)	5.24×10^{-4}	-	1.82×10^{-3}	0.934	1.14×10^{-4}	8.7×10^{-6}
radiative						

20.9 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 $1s^2$, the other elements of the group have a closed octet of electrons in their outer shell $ns^2 np^6$. 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 KrF_2 . Radon is a radioactive element and all its isotopes have very short half lives.



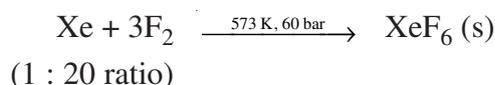
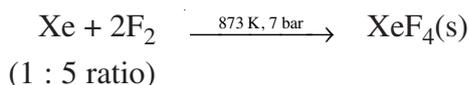
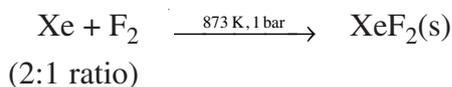
Notes



Notes

Xenon Compounds

Xenon reacts with fluorine to form binary fluorides, XeF₂, XeF₄ and XeF₆. The product formed depends on the temperature and xenon-fluorine ratio. Thus

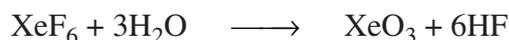


XeF₂, XeF₄ and XeF₆ are all white solids. They readily sublime at 298 K. They differ in their reactions with water

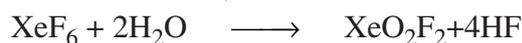
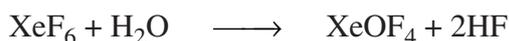
XeF₂ dissolves in water and undergoes slow hydrolysis in water.



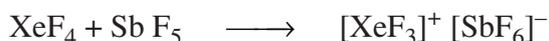
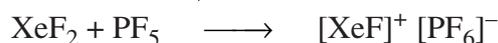
XeF₄ and XeF₆ react with water violently to give xenon trioxide and hydrogen fluoride.



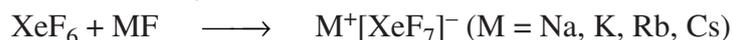
XeF₆ on partial hydrolysis gives, xenon oxofluorides.



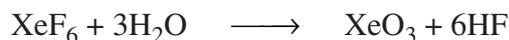
The xenon fluorides react with strong Lewis acids to form complexes.



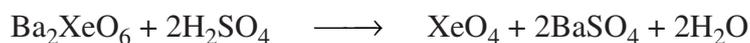
XeF₆ may also act as a fluoride acceptor from fluoride ion donors to form fluoroxenate anions.



XeO₃ can be prepared by hydrolysis of XeF₆



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



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.

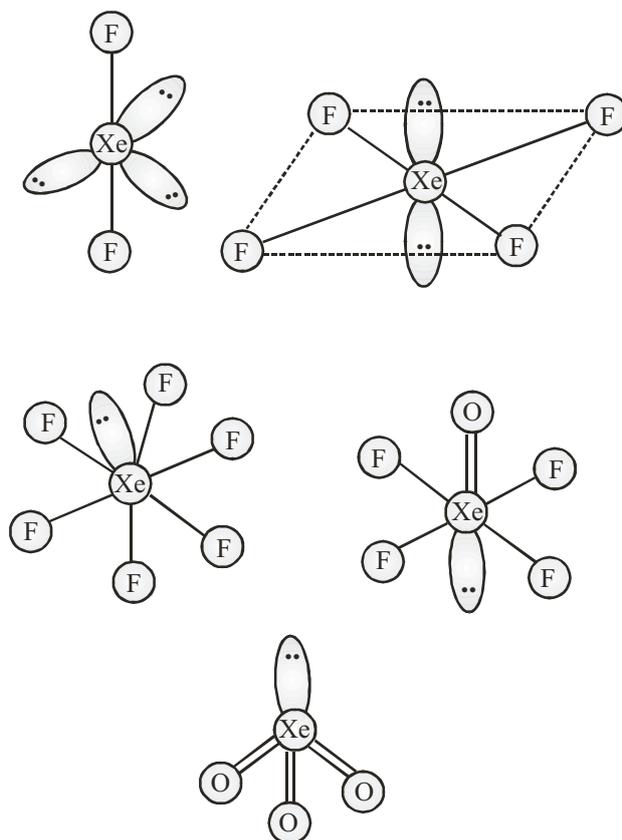


Fig. 20.3 : The structures of XeF_2 , XeF_4 , XeF_6 , XeO_3 and XeOF_4

**WHAT YOU HAVE LEARNT**

- General characteristics of the elements of Group 16, 17 & 18.
- 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.
- Allotropic forms of Sulphur preparation properties and uses of SO_2 .



Notes

MODULE - 6

Chemistry of Elements

p-block Elements and Their Compounds - II



Notes

- Sulphuric acid displays strong acid character and possesses oxidizing and dehydrating properties.
- Structure of oxoacids of Sulphur.
- Chlorine forms a number of oxoacids : HOCl , HClO_2 , HClO_3 and HClO_4 .
- 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 hydric acids.
- Fluorochlorocarbons are called freons which decompose ozone and are therefore environmentally hazardous.
- Occurance of noble gases.
- 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 : SO_2 , 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 SO_2 to SO_3 in the manufacture of sulphuric acid by contact process.
8. What is oleum?
9. Why is sulphuric acid known as king of chemicals?
10. Write down the structure of oxo acids of sulphur.

- Fluorine never acts as a central atom in any interhalogen compounds. Why?
- Draw the structure of BrF_4^- .
- Arrange the hydrogen halides in order of their acid strength in aqueous solution.
- Why is F_2O not known as fluorine oxide? Instead it is known as oxygen fluoride, OF_2 .
- Which is the strongest acid among the oxoacids of chlorine and why?
- What happens when XeF_4 reacts with SbF_5 ? Write the complete equation for the reaction.



Notes



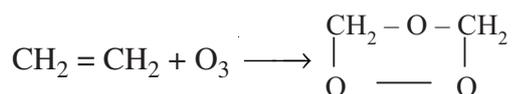
ANSWERS TO INTEXT QUESTIONS

20.1

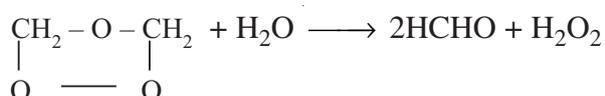
- Basic oxide : CaO ; acidic oxide : SO_2 ; amphoteric oxide : ZnO .
- Acidic oxide : $\text{SiO}_2, \text{SO}_2, \text{CrO}_3$
Basic oxide : $\text{K}_2\text{O}, \text{FeO}$
Amphoteric oxide : $\text{Al}_2\text{O}_3, \text{ZnO}$
- $\text{ZnO} + \text{H}_2\text{SO}_4 \longrightarrow \text{ZnSO}_4 + \text{H}_2\text{O}$
 $\text{ZnO} + 2\text{NaOH} \longrightarrow \text{Na}_2\text{ZnO}_2 + \text{H}_2\text{O}$
- An oxide of group 1, K_2O and of Gr 2 BaO
 $\text{K}_2\text{O} + 2\text{HCl} \longrightarrow 2\text{KCl} + \text{H}_2\text{O}$
 $\text{BaO} + \text{H}_2\text{SO}_4 \longrightarrow \text{BaSO}_4 + \text{H}_2\text{O}$
Oxygen has multiple bonds but sulphur has single bond.

20.2

When ethene combines with O_3 , an ozonide is formed, thus



On hydrolysis it gives HCHO ,



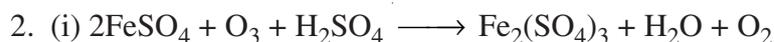
MODULE - 6

Chemistry of Elements

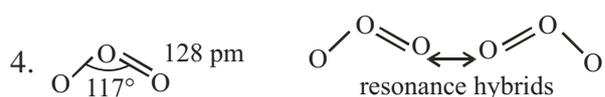
p-block Elements and Their Compounds - II



Notes



3. Ozone is 10 times more soluble than O_2 .



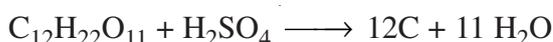
5. Mercury loses its convex meniscus and leaves a “tail” or a trail of minute droplets on a glass surface when exposed to ozone. This is due to the formation of mercurous oxide. The tailing effect can be removed by washing the mercury with a dilute acid.

20.3

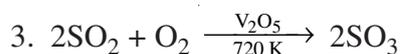
1 (i) Oxidizing property of conc. H_2SO_4



(ii) Dehydrating property : It removes water from sugar



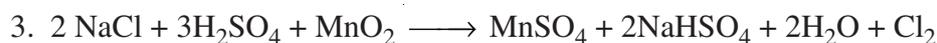
2. A corrosive mist of sulphuric acid is formed.



20.4

1. Fluorine

2. Fluorine



4. $\text{HI} > \text{HBr} > \text{HCl} > \text{HF}$

5. Chlorofluorocarbons (or freons)